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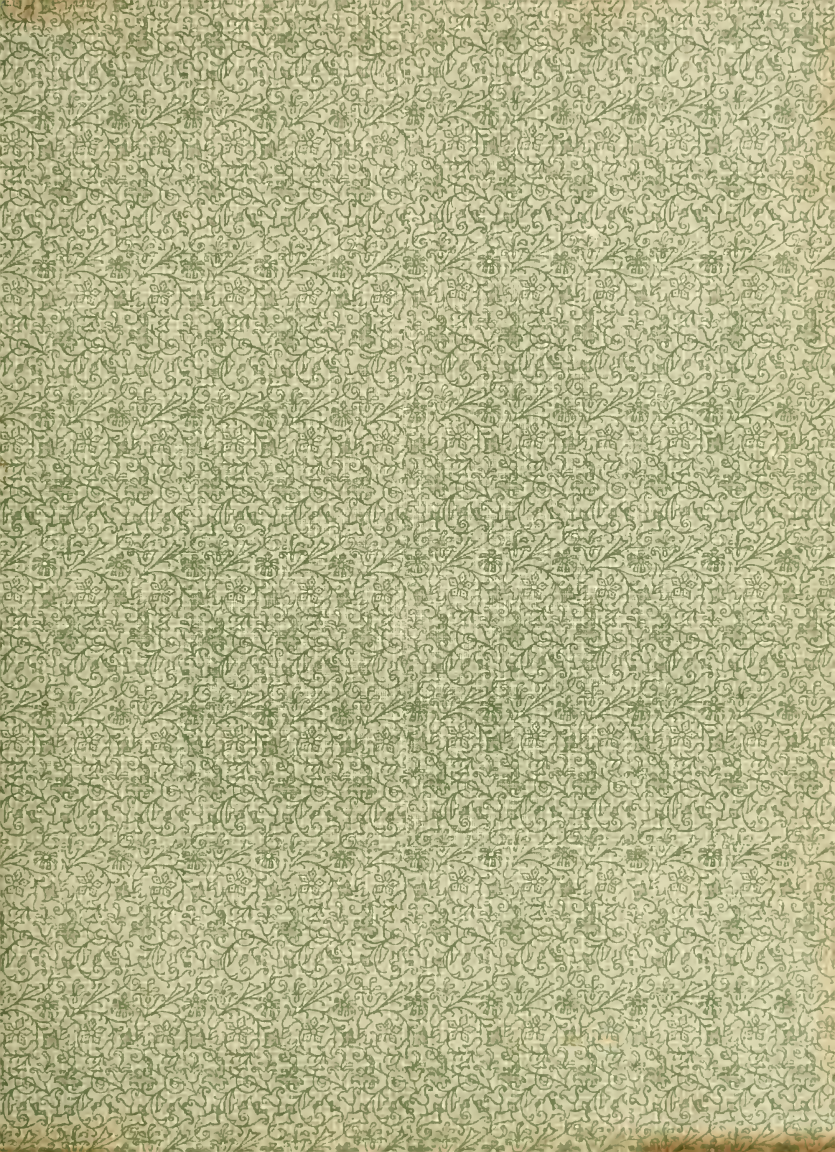
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A STUDY  
of the  
Conductivity of Certain Electrolytes in Water, Methyl  
And Ethyl Alcohols and Mixtures  
Of these Solvents;  
The Relation Between Conductivity and Viscosity.

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By  
Charles Reiger Carroll.

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DISSERTATION  
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES  
OF THE JOHN'S HOPKINS UNIVERSITY  
IN CONFORMITY WITH THE REQUIREMENTS FOR THE  
DEGREE OF DOCTOR OF PHILOSOPHY.

---

BALTIMORE

1904.





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# Introduction and Historical Review.

Before Arrhenius proposed his theory of electrolytic dissociation a number of investigations were carried out the aim of which was the study of the conductivities of non-aqueous solutions. Since the proposal of the theory there has been a still greater number of similar investigations. They are particularly interesting in the light of certain hypotheses as to the cause of the dissociating power of a solvent. To these hypotheses and to some of the work in non-aqueous solvents reference will be made in another part of this dissertation.

Much less has been done on conductivities in mixtures of solvents. A brief review of what has been done in this field is given.

(1)

Lenz measured the conductivities of various salts, potassium, iodide, bromide and chloride, sodium chloride, etc. in mixtures of methyl and ethyl alcohols and water.

Lenz found that in certain cases the relative resistances may be gotten from the equation

$$r = 100 ( 1 + b v ),$$



where 100 is taken as the resistance of an aqueous solution of ten parts per cent,  $v$  is the volume percent of alcohol, and  $a$ , a constant. The formula holds best for the mixtures of methyl alcohol and water.

(1)

Stephan<sup>1</sup> studied the conductivities of dilute solutions of sodium, potassium and lithium chlorides, and sodium and potassium iodides in mixtures of ethyl alcohol and water. His investigation of Stephan will be given a more detailed consideration in the second part of this dissertation.

(2)

Kabiukoff<sup>2</sup> determined the conductivity of hydrochloric acid in ethyl alcohol containing varying amounts of water.

(3)

Arrhenius<sup>3</sup> investigated the changes in the conductivity of aqueous solutions resulting from the addition to them of small quantities (less than 10% by volume) of non-electrolytes, such as methyl or ethyl alcohols, cane sugar, acetone, etc.

Arrhenius found that the changes could be expressed by the empirical formula

$$L = L_0 \left( 1 + \frac{a}{x} \right)^{-1}$$

where  $L$  is the conductivity in water,  $L_0$  that in the mixture,  $x$ , the volume percent of added non-electrolyte, and  $a$ , a constant peculiar to each non-electrolyte. Where two non-

(1). Wied. Abt. 17, 673, (1881).

(2). Ztschr. phys. Chem., 4, 131, (1897).

(3). Ztschr. phys. Chem., 9, 487, (1897).



electrolytes were added a similar empirical formula was found to hold. The coefficient  $\alpha$  differs not only for different nonelectrolytes and different electrolytes, but varies also with concentration, and is greatest when dissociation is least.

Arrhenius concludes that the amount of dissociation is not appreciably changed by addition of small quantities of nonelectrolytes. This follows from the fact that the alteration in conductivity is independent of the concentration. Further, he found that the velocity of inversion of cane sugar is not appreciably influenced by addition of small amounts of nonelectrolytes.

(1)

Holland worked in the same field as did Arrhenius.

(2)

His work will be referred to again. Strindberg repeated and confirmed some of Arrhenius' (loc. cit.) work.

(3)

Wakeman measured the conductivities of various electrolytes; sodium and potassium chlorides, hydrochloric acid, and numerous organic acids in mixtures of ethyl alcohol and water (containing 10, 20, 30, 40, and 50% alcohol).

For the cases studied the equation

$$\frac{\Delta}{p(100-p)} = \text{const.}$$

was found to hold, where  $\Delta$  is the difference between the

1. Wied. Ann. 50, 261, (1893).

2. Ztschr. Phys. Chem. 14, 111, (1894).

3. Ztschr. Phys. Chem. 11, 17, (1893).





conductivity of the electrolyte in water and in the mixture respectively, and  $p$  is the percent of alcohol by volume.

(1)

Small determined conductivities of picric acid in aqueous alcohol.

(2)

Zelinsky and Krapivin studied the conductivities of sodium and ammonium iodides and bromides in water, 50% alcohol, and a mixture of the two containing 50% of water by weight, for dilutions from  $v = 101$  to  $v = 10241$ .

Here a striking phenomenon was observed. The conductivities in the fifty percent mixture were found to be decided by less than the corresponding conductivities in the pure solvents. This minimum is best seen when the results are plotted as curves with the conductivities as ordinates and the composition of the mixture as abscissae.

(3)

Cohen observed the minimum in the case of potassium iodide. Cohen made a study of the conductivity of potassium iodide in mixtures of ethyl alcohol and water (containing 20, 40, 60, 80, and 99% alcohol). The dilutions ranged from  $v = 64$  to  $v = 2048$ . The minimum manifested itself in the 50% mixture from  $v = 512$  on.

(1) Ztschr. Phys. Chem., 14, 731, (1894).

(2) Ztschr. Phys. Chem., 21, 35, (1896).

(3) Ztschr. Phys. Chem., 25, 31, (1898).



from his observations and from those of Waksman (1898, 1899.) Cohen concludes that the relation  $\frac{\mu_{H_2O}}{\mu_{H_2O-Alc.}} = \text{constant value}$ , being independent of both temperature and concentration. That is, the conductivities compared are approaching a limiting value at the same rate, and either the dissociation is the same in the case compared, or, in the case of mixtures of alcohol and water, conductivity is not a direct measure of dissociation. Cohen inclines to the second view.

(1)

Walker and Hambly studied the conductivity of diethyl ammonium hydrochloride in mixtures of water and ethyl alcohol.

(2)(3)

Mantzsch made interesting applications of results obtained by studying conductivities in various mixtures.

(4)

Tijstra investigated the conductivities of solutions obtained by the action of mixtures of methyl or ethyl alcohol and water on sodium. In the case of the mixtures of ethyl alcohol and water the minimum was observed.

(5)

Potter made a careful study of the conductivity of potassium chloride in mixtures of ethyl alcohol and water con-

1. Jour. C. S. 71, 61, (1899).

(2). Ztschr. Anorg. Chem. 25, 352, (1900).

(3) Ber., 35, 1001, (1903).

(4) Proc. Kon. Akad. te Amsterdam. 1903, 104.

(5) Ztschr. Phys. Chem. 45, 403, (1903).



tainings and 20% alcohol by weight. He found that the relation given by Wakeham (loc.cit.) holds, while that given by Cohen (loc. cit.) was found not to hold. The quotient

$\frac{\mu_{H_2O}}{\mu_{H_2O} - Alc.}$ , was found to decrease with increasing dilution, and with increase of the amount of alcohol in the mixture. This, Roth thinks, may indicate a decrease in dissociation. The relation given by Arrhenius (loc. cit.) was also found to hold.

(1) (2)

The work of Wolf (1) and of Rudolf (2) needs no further consideration here.

(3)

Lindsay (3), extended the work of Zelinsky and Krapilwin and of Cohen. The solvents used were water, methyl, ethyl and isopropyl alcohols, and binary mixtures of these. The salts used were potassium, cadmium and strontium iodides, ammonium bromide and lithium nitrate. One result of Lindsay's work was to show that the minimum is more or less general.

Lindsay worked at two temperatures, 0° and 25°, and was able to show that in some cases, though the minimum does not occur at the higher temperature, it does occur at the lower temperature.

- 
1. Ztschr. Phys. Chem. 40, 222, (1903).
  2. Dissertation; Leipzig. (1903) and Ztschr. Phys. Chem.
  3. Dissertation; Johns Hopkins University. 1903. Amer. Chem. Journ. 28, 329, (1903).





He also showed the effect of variation of temperature upon the minimum, the effect being that rise in temperature shifts the minimum toward a mixture containing a larger percent of a conol.

The first part of this dissertation is a continuation of the investigations of Zelinsky and Krupin, of Cohen, and of Lindsay.



## I.

EXPERIMENTAL.Apparatus.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "Lan-  
 thanin". The resistance coils manufactured by Leeds & Co.  
 were guaranteed accurate to within one twenty-fifth of per-  
 cent. The conductivity cells were of the form used by  
 Lindsay. The constants of these were determined by means of  
 $N/50$  and  $N/500$  potassium chloride solutions. Cells used to  
 determine conductivities of the solvent and at high dilutions  
 were treated in the manner recommended by Whetnam<sup>(1)</sup>. The  
 electrodes were first coated with platinum black in the usual  
 manner, and were afterwards heated to a high temperature  
 in the flame of a blast lamp. It was found, as Whetnam states,  
 that the usual coating of platinum black, in spite of careful  
 and long continued washing, retains traces of salt that are  
 subsequently passed slowly into solution. The oxidizing  
 action of the platinum black is also thus avoided. For the  
 purposes mentioned electrodes of this kind cannot be too highly  
 recommended. The tone-minimum in the telescope is fully as

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(1). Phil. Trans. 34 (A), 321, (1900);  
 Ztschr. Phys. Chem. 52, 346, (1900).



used as with the ordinary type of electrode.

The twenty five degree bath was of the Desautel (Desautel) form and was stirred by a small hot-air motor.

The zero bath was of the type used by Lindsay consisting of an outer and inner vessel. The annular space between the two, and the inner vessel were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel about an equal weight of water was added. By the foregoing means the temperature of a cell immersed in the ice and water of the inner vessel could be kept for any desired period of time at  $0^{\circ}.02$  to  $0^{\circ}.05$ .

The measuring flasks, pipettes and burettes were carefully calibrated.

Solvents. The water used was purified in the following manner; Ordinary distilled water, after addition of potassium dichromate and sulphuric acid, was redistilled. The distillate was again distilled from chromic acid into, and then from, a solution of barium hydroxide. Where the conductivity of the water thus obtained was above  $2 \times 10^{-6}$ , it was redistilled. In many cases the conductivity was much less than this value.

The methyl and ethyl alcohols were the purest commercial preparations obtainable. Each was subjected to the same



treatment. The alcohol was dehydrated by standing in contact with freshly burned lime for several weeks. From this it was distilled and then allowed to stand over dehydrated copper sulphate for a week or more. As required for use, it was distilled from the copper sulphate, small quantities of sodium being added, and precautions being taken to protect the distillate from access of moisture.

The conductivity of the methyl alcohol thus obtained was usually from  $1 - 4 \times 10^{-6}$ . That of the ethyl alcohol was less than this.

The acetic acid used was obtained from Bender and Hoebein and was designed for cryoscopic work. The amount of water contained in it was determined, as suggested by Rüdorff, by observation of its freezing point. Its conductivity was less than  $2 \times 10^{-6}$ .

#### Method of preparing the solutions.

The mixtures of solvents were prepared as follows. 10 c c of alcohol, for example, were diluted to, say, 100 cc. This is designated as a mixture of "n" percent alcohol.

In making the dilutions calibrated flasks were used, and the temperature was kept to within a few tenths of a degree of the temperature of calibration.





In making up the solutions, the exact amount of the weight in question was put into a weighed flask, and after addition of a portion of the solvent and solution of the substance the flask was filled to the mark. Where also the temperature was kept under control.

Usually the original solutions were  $N/16$  or  $n/32$ . From the original solution, further solutions were made by adding solvent to a measured portion of the solution. Where the quantity to be used would be too small to be measured with reasonable accuracy, one of the intermediate solutions was taken as a starting point for further dilutions.



Conductivity measurements.

The conductance of the cells used were determined or checked at intervals of a few days. For each determination from three to seven or eight different resistances were used. The values given in the tables are, therefore, the mean of several determinations. Conductivities throughout are molar conductivities.

Cadmium Iodide.

The cadmium iodide used was a preparation from Kahlbaum used by Lindsay in his work.

Lindsay measured the conductivity of cadmium iodide in water, methyl alcohol and mixtures at 25 only. The minimum was not observed. It seemed desirable, therefore, to complete the study of the compound.

The cadmium iodide was dried by being allowed to stand in a desiccator over calcium chloride for a week or more. At first the attempt was made to dry it by long continued heating in an air-bath at 70° - 80°. It was found that when thus treated the salt assumed a pinkish tinge, which immediately gives place to the pinkish-white of the salt in the ordinary condition, when traces of water are added. No mention of this color change can be found in the literature. Though no traces of decomposition could be detected, for safety's sake of drying was chosen.

The original solutions were made by direct weighing.



Table 1. Conductivity of Cd  $I_2$  in water at 0° and at 25°.

v	0°	25°	c
16	31.15	64.36	1.250
32	40.07	81.82	1.670
64	51.93	107.77	2.111
128	63.15	130.24	2.606
256	76.34	155.55	3.100

The temperature coefficient, or the change in conductivity for one degree change in temperature is indicated by the symbol c.

Table 2. Conductivity of Cd  $I_2$  in 25%  $CH_3OH$  at 0° and at 25°

v.	0°	25°	c.
16	14.57	33.93	0.770
32	17.08	42.10	0.777
64	22.05	55.02	1.294
128	29.39	70.22	1.665
256	35.36	87.31	2.672

Table 3. Conductivity of Cd  $I_2$  in 50%  $CH_3OH$  at 0° and at 25°.

v	0°	25°	c
16	9.96	20.82	0.731
32	11.23	27.31	0.519
64	14.31	31.25	0.282
128	15.92	41.51	0.705
256	17.54	51.4	1.195



Table 4. Conductivity of Cd  $I_2$  in 75%  $CH_3OH$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	c
16	8.94	13.78	0.294
32	9.71	17.08	0.275
64	11.24	20.09	0.334
128	14.37	25.68	0.452
256	18.58	33.58	0.598

Table 5. Conductivity of Cd  $I_2$  in 100%  $CH_3OH$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	c
16	10.96	13.39	0.097
32	11.55	14.51	0.118
64	12.66	14.83	0.087
128	13.69	16.82	0.124
256	17.62	20.01	0.096

Table 6. Comparison of Conductivities at  $0^\circ$ .

v	0%	25%	50%	75%	100% $CH_3OH$
16	31.16	14.57	9.96	8.94	10.96
32	40.07	17.68	11.23	9.71	11.55
64	51.93	22.68	14.21	11.28	12.66
128	62.53	31.09	17.92	14.37	14.69
256	76.54	35.31	21.58	18.58	17.62





Table 7. Comparison of Conductivities at 25°.

v	0.1	0.5	1.0	7.5	100% Cd SO <sub>4</sub>
16	44.85	33.33	20.84	15.78	12.39
32	81.84	42.10	32.21	17.08	14.51
64	104.77	55.02	31.25	20.08	14.83
128	130.22	70.22	41.11	23.37	16.82
256	172.35	87.31	51.40	33.32	20.01

Table 8. Conductivity of Cd I<sub>2</sub> in 25% C<sub>2</sub>H<sub>5</sub>OH at 25°.

v	Conductivity
16	26.97
32	31.30
64	44.24
128	54.54
256	69.71

Table 9. Conductivity of Cd I<sub>2</sub> in 50% C<sub>2</sub>H<sub>5</sub>OH at 25°.

v	Conductivity
16	14.05
32	16.19
64	18.93
128	22.86
256	34.59



Table 10. Conductivity of Cd I<sub>2</sub> in 75% C<sub>2</sub>H<sub>5</sub>OH at 25°.

v	
16	9.43
32	9.52
64	10.94
128	12.27
256	15.16

Table 11. Conductivity of Cd I<sub>2</sub> in 100% C<sub>2</sub>H<sub>5</sub>OH at 25°.

v	
16	2.29
32	2.30
64	2.32
128	2.39
256	2.56

Table 12. Comparison of Conductivities at 25°.

v	0%	25%	50%	75%	100%
16	12.86	21.97	14.03	9.43	2.29
32	81.22	34.90	16.19	9.52	2.30
64	104.77	44.21	17.93	10.94	2.32
128	130.24	54.31	20.66	12.27	2.39
256	155.45	69.71	34.89	15.16	2.56



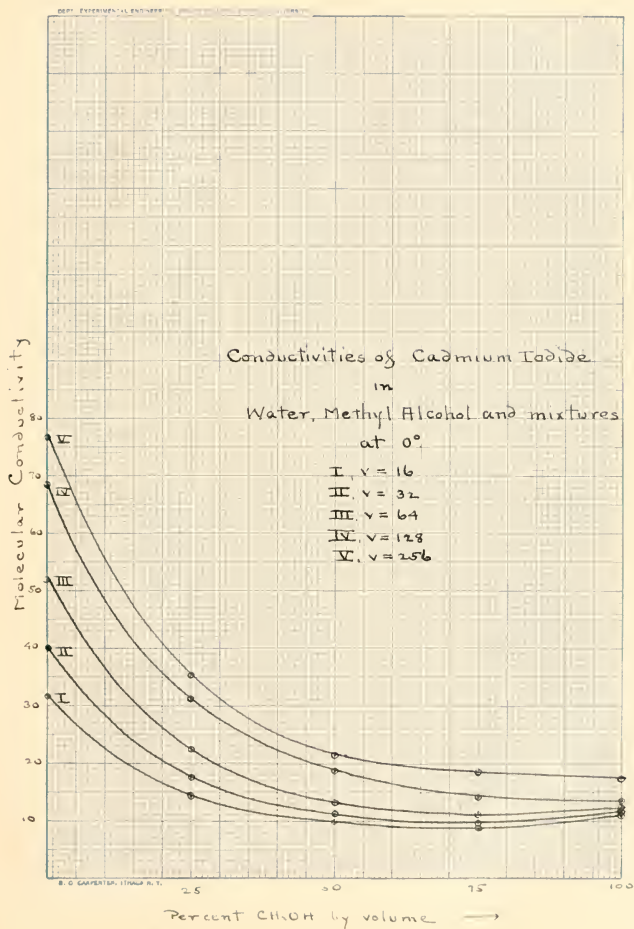


Fig. I



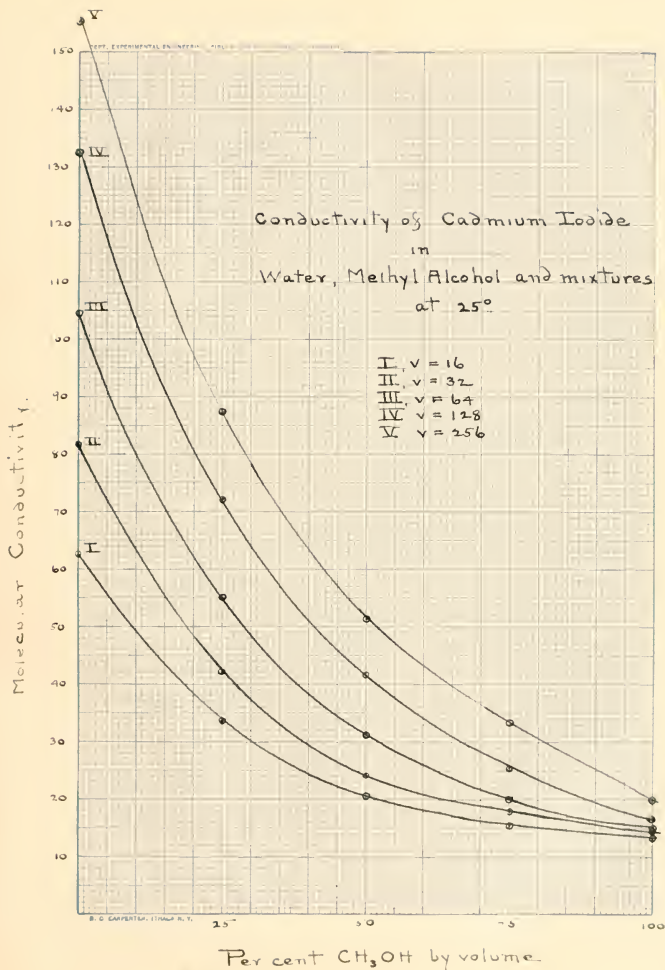


Fig II





From the data given, essentially in table 1, and Fig. I it is seen that cadmium iodide does not show the minimum in mixtures of methyl alcohol and water at 25°. At 0° however, in a forty five percent mixture, at volumes 14, 32 and 48, the minimum appears. Beyond these dilutions it does not appear.

In various mixtures of ethyl alcohol and water at 25° (Table 12), no minimum appears, though the values observed are in all cases less than would be expected from the rule of averages.

The results have been plotted as curves in Figs. I and II, the ordinates being conductivities, the abscissae representing the percent by volume of alcohol.

#### Sodium iodide.

The sodium iodide used was a preparation that had been carefully purified by Lindsay.

The salt was dried in an air-bath for three days, at a temperature of 110°- 130°. This prolonged treatment was found necessary to bring it to constant weight.

The original solutions were made up by direct weighing.



Table 13. Conductivity of Na I in water at 0° and at 25°

v	0°	25°	$\kappa$ (C)	c
32	57.46	106.0	105.7	1.942
64	59.37	109.35	109.3	2.000
128	60.71	112.44	112.3	2.069
256	62.35	115.5	115.2	2.126
512	64.29	118.08	117.9	2.182

The values in the last column are those given by Ostwald (Lehrbuch, II (1914) 353). The agreement is seen to be quite satisfactory.

Table 14. Conductivity of NaI in 25% CH<sub>3</sub>OH and at 25°.

v	0°	25°	c
32	33.65	70.62	1.48
64	34.68	72.77	1.52
128	35.63	73.78	1.53
256	36.73	74.33	1.504
512	37.83	74.38	1.49

The values for 0 are uncorrected for the conductivity of the solvent.

Table 15. Conductivity of Na I in 50% CH<sub>3</sub>OH at 0° and at 25°.

v	0°	25°	c.
32	27.1	56.18	1.171
64	28.75	58.30	1.185
128	29.61	59.16	1.203
256	30.32	60.37	1.221
512	31.05	61.00	1.231



Table 16. Conductivity of Na I in 100%  $\text{CH}_3\text{OH}$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	c
32	31.70	16.50	0.332
64	33.08	69.17	1.086
128	34.16	41.49	1.003
256	34.72	52.04	1.121
512	35.00	63.77	1.151

Table 17. Conductivity of Na I in 100%  $\text{CH}_3\text{OH}$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	c
32	51.09	72.03	0.838
64	55.95	77.63	0.867
128	58.89	82.76	0.955
256	61.02	86.19	1.009
512	62.56	89.27	1.028

Table 18. Comparison of Conductivities at  $0^\circ$ .

v	0%	15%	50%	75%	100% $\text{CH}_3\text{OH}$
32	57.16	33.63	27.31	31.70	51.09
64	59.37	34.63	28.75	33.08	55.95
128	60.71	35.63	29.04	34.16	58.89
256	62.32	36.73	30.32	34.72	61.02
512	64.28	37.83	32.08	35.00	62.56



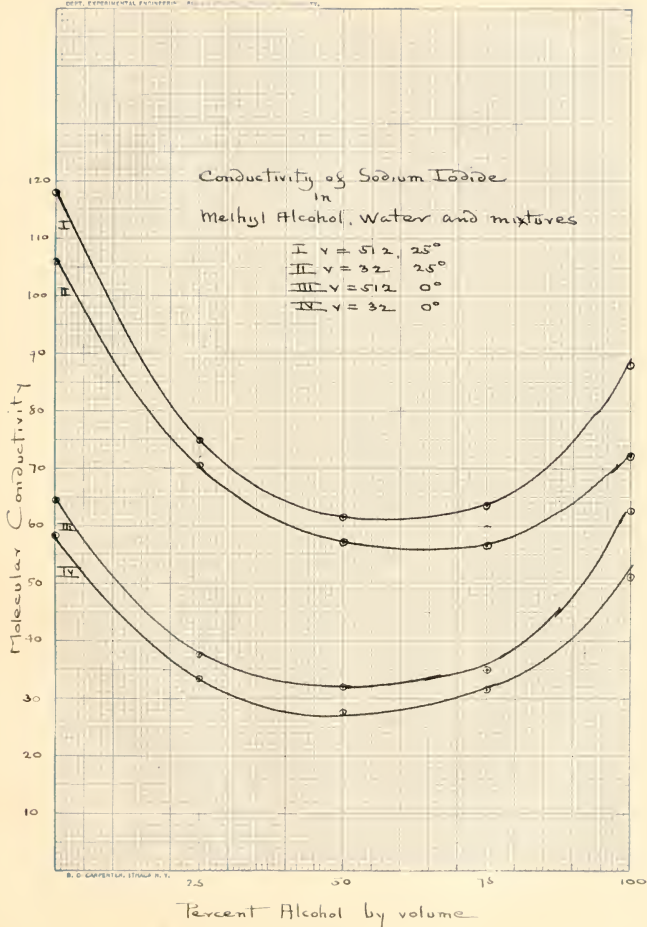


Fig. III.





Table 1. Refractive Index of Ethyl Alcohol-Water at 25°.

v	0%	33%	50%	66%	100%
32	100.0	70.63	57.13	38.50	72.03
64	109.33	72.77	58.50	39.47	77.63
128	112.44	73.79	59.16	41.19	82.70
256	115.49	74.33	60.37	42.72	88.19
512	118.08	74.98	61.63	43.77	93.27

From the data given, table 18 and 19, and from the curves plotted in the manner indicated (Fig. III), it is evident that sodium iodide exhibits the minimum in mixtures of ethyl alcohol and water. Only two dilutions at the two temperatures of observation have been plotted. The curves would be too close together if all were plotted.

The minimum, as Lindsay has observed, is more pronounced at 0° than at 25°. Further, the shifting effect of change of temperature and of concentration, also observed by Lindsay, appears at 25°,  $v = 32$ . The minimum occurs in a 75% mixture, beyond this dilution, the minimum shifts slowly to the 50% mixture. At 0° the minimum is shifted to the 50% mixture more.



Calcium nitrate.

To substantiate our study of a ternary salt-water system, Lindsay had already made a study of strontianite. Lindsay also found it to exhibit the same phenomena as did binary salts.

The calcium nitrate used was a preparation from Karlsruhe. It was found to be particularly difficult to dehydrate. Ventilation for several days at a temperature of 130 - 140 was necessary to bring it to constant weight. This treatment caused no perceptible decomposition. All original solutions were made by direct weighing.

Table 20. Conductivity of Calcium nitrate in water at 0° & 25°

v	0°	25°	c.
16	97.33	117.36	3.339
32	102.17	121.45	3.410
48	106.35	125.34	3.481
128	113.59	129.93	3.554
256	118.00	135.93	3.616

Table 21. Conductivity of calcium nitrate in 10% CH<sub>3</sub>OH at 0° and 25°.

v	0°	25°	c.
16	55.17	111.45	2.831
32	59.30	120.83	2.928
48	63.51	128.35	2.998
128	68.36	140.11	3.131
256	70.15	147.11	3.190



Table 25. Conductivity of Calcium Nitrate in 95%  $\text{CH}_3\text{OH}$  at  $0^\circ$  and at  $25^\circ$ .

$\nu$	$0^\circ$	$25^\circ$	$\kappa$
16	41.07	89.04	1.318
32	41.70	90.11	1.316
48	41.13	89.31	1.316
100	53.34	103.68	1.390
150	47.32	109.19	1.445

Table 26. Conductivity of Calcium Nitrate in 72%  $\text{CH}_3\text{OH}$  at  $0^\circ$  and at  $25^\circ$ .

$\nu$	$0^\circ$	$25^\circ$	$\kappa$
16	33.39	70.06	1.316
32	43.60	80.16	1.402
48	48.85	89.98	1.481
100	51.40	87.73	1.483

150

Table 27. Conductivity of Calcium Nitrate in 100%  $\text{CH}_3\text{OH}$  at  $0^\circ$  and at  $25^\circ$ .

$\nu$	$0^\circ$	$25^\circ$	$\kappa$
16		12.79	
32	27.30	41.82	0.823
48	27.27	40.99	0.811
100	27.11	40.73	0.800
150	27	42.10	0.823



Table 25. Comparison of conductivities at 0°.

v	0%	45%	90%	75%	100%
10	29.32	23.15	21.01	23.37	
20	104.47	57.50	42.50	43.00	51.50
30	109.45	59.81	42.15	44.85	57.37
120	113.53	63.39	52.92	51.50	66.66
150	118.02	69.11	54.82		70.47

Table 26. Comparison of conductivities at 25°.

v	0%	45%	90%	75%	100%
10	177.36	113.45	79.04	70.04	52.79
20	189.45	120.83	80.11	80.16	61.58
30	199.34	128.9	94.55	89.37	70.73
120	209.93	136.11	105.12	97.72	80.32
150	215.93	141.11	109.19		75.98

Table 27. Conductivity of Calcium Nitrate 34.25%  $\text{Ca}(\text{NO}_3)_2$  at 0° and at 25°.

v	0°	25°	
10	32.80	32.93	2.03
20	41.57	40.93	0.64
30			
120	46.03	44.93	1.10
150	50.41	49.01	.78





Table 10. Conductivity of calcium nitrate in 10%  $C_2H_5O$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	$\kappa$
16	13.7	40.83	1.809
32	28.89	85.50	1.891
64	47.37	139.83	1.878
128	68.83	211.15	1.861
256	90.50	297.51	1.840

Table 11. Conductivity of calcium nitrate in 75%  $C_2H_5O$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	$\kappa$
16	19.15	59.08	0.795
32	41.41	111.57	0.821
64			
128	48.71	56.08	1.175
256	48.81	60.79	1.281

Table 12. Conductivity of calcium nitrate in 100%  $C_2H_5O$  at  $0^\circ$  and at  $25^\circ$ .

v	$0^\circ$	$25^\circ$	$\kappa$
16	8.89	7.08	0.6
32	7.11	8.59	0.681
64	9.89	12.12	0.133
128	10.34	78.49	0.189
256	12.11	58.17	0.211



Table 31. Comparison of conductivities at 0°.

v	0%	25%	50%	75%	100%
16	34.33	23.0	23.7	19.13	4.3
32	104.47	41.34	25.39	21.41	7.11
48	108.35		27.37		1.32
140	113.59	48.02	28.83	26.71	10.74
150	118.04	50.26	30.30	28.61	12.48

Table 32. Comparison of conductivities at 15°.

v	0%	25%	50%	75%	100%
16	177.56	92.93	60.43	39.08	7.03
32	189.43	100.56	65.30	41.57	9.57
48	197.31		69.03		12.13
128	207.03	113.93	71.13	56.03	15.47
150	213.93	119.04	75.31	60.79	17.37

From the data given tables 25, 26, 31, 32, and from inspection of the conductivity curves, it is evident that calcium nitrate in no case exhibits the minimum. The conductivities are always less than the other series.

The relation found by Winkler (loc. cit.)  $\frac{\Delta}{r(100-r)}$  = const. does not hold in the cases thus far studied. Nor does that found by Cohen (loc. cit.)



### Hydrochloric acid.

In the study of hydrochloric acid the solutions were made as follows. The solvent was prepared in the usual manner. Into a portion of the solvent, kept cool by ice, dry hydrochloric acid gas was passed. This was obtained by allowing concentrated sulphuric acid to fall slowly from a dropping funnel into pure, aqueous, hydrochloric acid. The gas was dried by passing through two gas-washing bottles containing concentrated sulphuric acid. The vessel containing the solvent into which the gas was passed was protected from extraneous moisture by a drying tube containing phosphorus pentoxide.

From the original solution thus prepared the dilutions were prepared. The strength of the original solution was determined volumetrically by means of a standard solution of ammonium hydroxide, metyl orange being used as an indicator. Control determinations were made on some of the dilutions, since only somewhat dilute solutions in mixtures and in pure methyl alcohol were found to be stable.

The composition of the 69.75% mixture was determined by means of its specific gravity.



Table 33. Conductivity of HCl in 50%  $\text{CH}_3\text{OH}$  at 25°.

$\nu$	
33.054	172.43
132.308	166.09
264.416	163.30
528.832	155.29

Table 34. Conductivity of HCl in 69.75%  $\text{CH}_3\text{OH}$  at 0° & 25°.

$\nu$	0°	25°
17.67	63.83	116.0
92.43	67.06	123.77
178.75	66.49	117.8
357.5	64.66	118.1
714.72	66.19	116.87

Table 35. Conductivity of HCl in 90%  $\text{CH}_3\text{OH}$  at 0 and at 25°.

$\nu$	0°	25°
31.535	46.39	73.79
63.07	47.60	76.19
127.175	51.34	84.27
252.35	51.84	84.27
252.35	51.35	84.35
504.50		84.22





Table 35. Conductivity of HCl in 100% CH<sub>3</sub>OH at 0° and at 25°.

v	0°	25°
9.125	67.36	95.83
22.8	77.05	110.50
130.2	79.84	111.79
481.44	80.79	129.27
2104.	85.46	133.44

A consideration of the results, tables 33, 34, 35, 36, shows that in certain cases the results are irregular and unexpected. In the 50% mixture the conductivity falls from the first dilution, which is analogous to what has been observed for hydrochloric acid in ether and isocetyl alcohol by Cattaneo (1) and Kablukoff, (2) and for sulphuric acid in acetic acid by Jones (3). In all these cases the molar conductivities decreased with decreasing dilution.

In the 69.75% a maximum is reached at  $v = 92.42$  at 0° and 25°. From this point on the conductivities fall slightly. However, at 0° the mean of the four last conductivities, including the maximum, differs from the maximum value by only one and one-half percent.

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- (1). Atti. R. Acc. delle Sc., Torino, 28, 329.  
Rend. R. Accad. dei Lincei. (5), 1, 295.  
(2). Ztschr. Phys. Chem., 4, 431, (1899).  
(3). Ann. Chem. Phys., 10, 1, (1894).



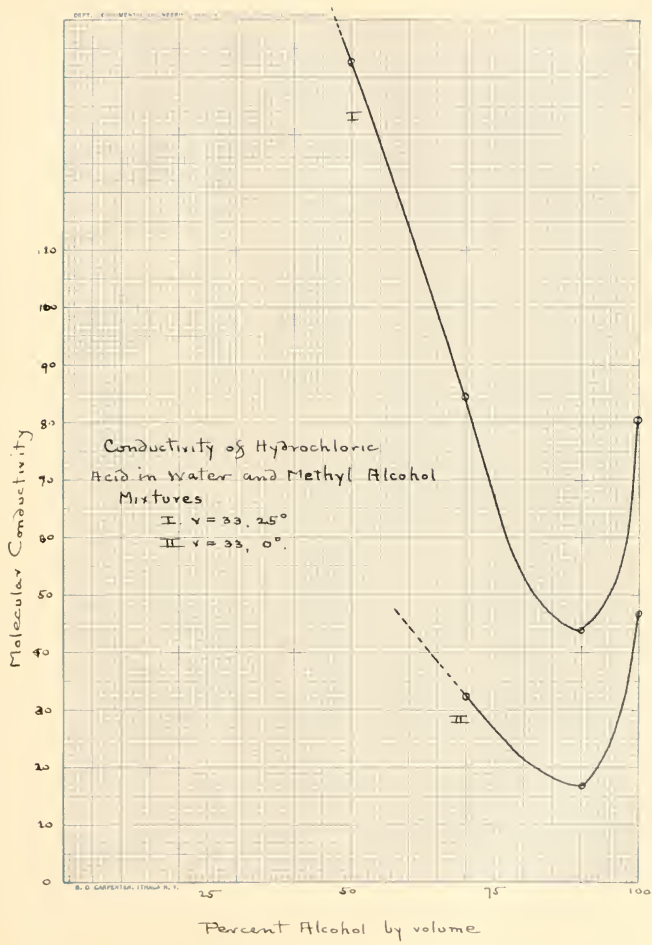


Fig IV



In 90% mixture the results are perfectly regular, and, what is surprising, a minimum value is reached at  $v = 157.672$ .

In ethyl alcohol the results are also regular, but there is no indication of a maximum value for conductivity. The values found agree in most cases very well with those of (1) Carrara. Carrara's results are also irregular.

It is seen further that hydrochloric acid shows a minimum (Fig. IV) in both the 69.75% and 90% mixtures. At 25 the minimum appears in the former after the dilution  $v = 178.75$ . At 0° it appears at all dilutions. Carrara (loc. cit.) has also observed the minimum in the case of hydrochloric acid, finding it to occur in ethyl alcohol containing about two percent of water.

I have plotted the conductivity curves (Fig. IV) for  $v = 33$ .

#### Sodium Acetate in Mixtures of Acetic Acid and Water.

Thus far we have been concerned with conductivities in mixtures of alcohol and water. An investigation by Jones and Murray (2) seemed to make it advisable to study conductivities in other mixtures - notably of acetic or formic

(1) Gazz. chim. It. 36 (1), 187, 1876.

(2) Amer. Chem. Journ. 30, 183, (1896).



acids and water. The connection of the two investigations will be considered when we come to discuss the nature of the mechanism.

As stated the acetic acid used was a preparation intended for cryoscopic work. The amount of water in this acid was determined by means of its freezing point, as recommended by (1) Rüdorff. The substance froze at  $15.47^{\circ}$ . As calculated from the tables given by Püdorff (loc. cit.) it contained in 100 parts by weight 0.6 parts of water by weight. Knowing the composition of the acid, the proper amounts to be used in making the mixtures could be determined.

A portion of the acid was partially frozen and the still liquid portion was rejected. After melting the solid acid, the process was repeated. The specimen thus obtained was used for the conductivities in the pure solvent. Owing to inevitable exposure to moisture of the air it was not thought profitable to try to remove the last traces of moisture.

In this part of the problem new complications arise, since acetic acid in aqueous solution conducts the current.

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(1) Z. Ber., 3, 340, (1870).









Table 9. Conductivity of sodium acetate in 75% acetic acid at 25°.  
Specific conductivity, 0.001.

$\nu$	sp. cond.	
32	0.7020	20.7
64	0.4416	21.2
128	0.2929	21.4

Table 10. Conductivity of sodium acetate in acetic acid, at 25°.  
Conductivity  $1 \times 10^{-6}$ .

$\nu$	sp. cond.	
32	0.00412	0.134
64	0.00236	0.161
128	0.00129	0.165

On examination the results are seen to be irregular and no conclusions can be drawn from them. In the 75% mixture the molecular conductivity is apparently negative. This, of course, means nothing more than that the specific conductivity of the solvent is greater than that of the solution. Only in the 75% mixture is there any regularity observed. Here the (apparent) molecular conductivities increase with decreasing concentration.

In the pure solvent the conductivities are so small as to be almost negligible. This is not surprising. (2)

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(1). Ztschr. f. phys. Chem. 11, 111, (1914).



has determined the conductivity of hydrochloric acid in acetic acid and has found it to be exceedingly small.

For example, for  $\nu = 38.56 \mu$  was found to be 1.73.

The irregular results of mixtures of acetic acid and water are to be explained as being due to mutual isomeric influence of dissolved substance and solvent. The dissociation of the sodium acetate is driven back by the presence of the acetic acid, and vice versa. This influence is most marked where the dissociation of each separately would be greatest, i. e., in mixtures of lower percent of acetic acid, and of minimal concentration of sodium acetate.

Since these phenomena have no direct connection with the problem in hand no further discussion is necessary, and particularly since the question has been treated by Wolf (loc. cit.) and by Rudorff (loc. cit.).



### Dissociation in $10\% \text{CH}_3\text{OH}$ .

It has been seen that in the case of oxoacetic acid in mixtures of methyl alcohol and water limiting values for conductivity are reached at a less dilution than in either water or methyl alcohol. It is important to see whether this is a particular or a general phenomenon.

The limiting values in the case of sodium and potassium iodides, and potassium bromide were determined. Throughout this part of the work the utmost care was taken in the preparation of solvents and solutions and in making the dilutions. The cells used were standardized before and after each series of measurements. The conductivity of the solvent was carefully determined and the necessary corrections were made. The water and the methyl alcohol used had a conductivity of not over  $1 \times 10^{-6}$ . All values are the mean of from five to ten different values.

Potassium iodide. The potassium iodide was a preparation furnished by Kahlbaum. The flame test showed that no impurity was present. The salt was dried at  $100^\circ - 110^\circ$  for a day. The values obtained were

v

100	69.20
1000	70.58
10000	70.80





For values of  $\kappa$  for  $\text{KIO}_3$  at  $v = 100$  (approximate) (interpolated) value obtained by Zelinsky and Fraumeni (loc. cit.) and by results may therefore be interpreted as to trends. This has been done in the following table. The degree of association has been calculated for each solution. The used 10 and 100 mole for comparison are similar values calculated from data given by Ostwald (1) for potassium iodide in water, and from Carrara (loc. cit.) for potassium iodide in methyl alcohol.

Table 11. Conductivity of potassium iodide in water, methyl alcohol, and 50% methyl alcohol.

$v$	$\text{H}_2\text{O}$	$\text{CH}_3\text{OH}-50\%$	$\text{CH}_3\text{OH}$
10	124.5	62.13	67.14
32	126.5	64.37	69.42
54	130.5	66.01	70.95
100	133.0	67.15	72.78
150	134.8	68.28	74.22
200		69.30	
342	137.9	73.65	76.81
1000	140.0	76.35	78.67
1000		76.38	
1000		76.60	
$\infty$	142.0	76.80	79.13



the values of the dissociation constant are given in the following table. From a comparison of the data it is seen that the  $K_a$  values for conductivity in measured at a lower dilution in the mixture than in the other solvents.

Table 13. Dissociation of perchloric acid in water, 90% ethanol, and 100% wet yl alcohol.

$\nu$	$\times 10^3$	$\times 10^3$ $\text{OH}_3\text{OH}$	$\times 10^3$ $\text{H}_2\text{O}$
10	0.870	0.980	0.890
30	0.900	0.910	0.89
40	0.910	0.930	0.910
120	0.931	0.950	0.960
206	0.943	0.968	0.904
510	0.967	0.987	0.931
1030	0.989	1.000	0.954

An inspection of this table shows that at corresponding dilutions dissociation as calculated from conductivity is greater in the mixture than in wet yl alcohol or in water. The only other solvent thus far shown to have a greater dissociation than water is liquid hydrocyanic acid, as appears from the work of Centnerszwer<sup>(1)</sup>. Perchloric acid is one of the advantages used.

(1) Zeitschr. Chem. Phys. 33, 217, (1904).



sodium iodide. The  $\kappa_{\infty}$  of iodide was determined practically used. The following measurements were made.

v	$\kappa_{\infty}$
500	60.92
1000	61.72
1500	61.85

Comparing these with the values previously obtained by us and using Carrara's (loc. cit.) values for conductivities in water and methyl alcohol respectively, we have the following.

Table 13. Conductivity of sodium iodide in water, methyl alcohol, and 50% methyl alcohol.

v	H <sub>2</sub> O	50% CH <sub>3</sub> OH	CH <sub>3</sub> O H.
32	106.0	57.18	46.75
64	109.3	58.30	73.11
128	112.4	59.16	77.31
256	115.5	60.87	79.00
512	118.1	61.27	82.25
1000		61.72	
1500		61.85	
$\infty$	121.4 (0)	61.85	83.77

It is evident that in this case the results are the same in form found for potassium iodide.



Table II. Dissociation of sodium iodide in water, 50% alcohol, and 50% methyl alcohol.

$v$	$\alpha$ in $H_2O$	$\alpha$ 50% $CH_3OH$	$\alpha$ $CH_3OH$ .
32	0.855	0.927	0.782
64	0.901	0.946	0.816
128	0.917	0.959	0.861
256	0.949	0.987	0.896
512	0.971	0.993	0.915
2000		1.000	
4000	1.000	1.000	

There also, as was found for potassium iodide, the dissociation is greatest in the mixture.

The following measurements were made for potassium bromide in 50%  $CH_3OH$ .

$v$	
128	87.78
256	89.36
512	89.35

At  $v = 128$  the dissociation is 0.949 for the mixture.

At  $v = 256$  the dissociation is 0.937 for water, calculated from Ostwald's (loc. cit.) and Barrara's values.





Table 43. Dissociation of Ammonium bromide in 30%  $\text{CH}_3\text{OH}$ and 1- $\alpha$ - $\text{CH}_3\text{OH}$  25°.

$\nu$	$\alpha$ - $\text{CH}_3\text{OH}$ 30%
16	0.971
32	0.910
64	0.842
128	0.902
256	0.974
512	0.986
1024	1.000

The values for the dissociation constants are seen to be about the same as those for potassium iodide. Data for conductivity in aqueous solution could not be found. The values for  $\text{CH}_3\text{OH}$  are calculated from Carrara's (loc. cit.) data. Those for the mixture from Zelinsky and Kravitski's data.

Table 44. Dissociation of Ammonium iodide in 30%  $\text{CH}_3\text{OH}$  and $\text{CH}_3\text{OH}$ .

$\nu$	$\alpha$ - 30% $\text{CH}_3\text{OH}$ .
16	0.975
32	0.909
64	0.913
128	0.917
256	0.973
512	0.994
1024	1.000



where the values are known, or available for a similar compound. No data could be found for ammonium iodide in  $\text{CH}_3\text{OH}$ . The data for the mixture and for  $\text{CH}_3\text{OH}$  were furnished by Zelinsky and Krupavich and by Carrara respectively.

From data given by Lindsay it is possible to calculate the dissociation of Lithium Nitrate in the 90% mixture at two temperatures 0 and 25°, assuming that there is in the other cases complete dissociation is reached at  $v = 1024$ . It is known that in aqueous solution complete dissociation is not reached so soon in the case of Lithium salts as in the case of potassium or sodium salts. A lesser value must therefore be attached to the following.

Table 47. Dissociation of Lithium nitrate in 90%  $\text{CH}_3\text{OH}$  at 0° and at 25°.

$v$	$\alpha = 0^\circ$	$\alpha = 25^\circ$
32	0.863	0.862
64	0.899	0.899
128	0.915	0.920
256	0.924	0.924
512	0.925	0.925
1024	1.000	1.000

Values of the dissociation constants for hydrochloric acid in the 90% and in the 99.79% mixture is 0 and 0.01 respectively.



shown. It will be remembered that the results in the latter mixtures were irregular. No stress can therefore be put on the figures for that mixture. I have taken the values for  $\alpha = 23.4$  as the limiting values in this case.

Table 19. Dissociation of hydrochloric acid in 69.75% and 90%  $\text{CH}_3\text{OH}$ , in water, and in  $\text{CH}_3\text{OH}$ .

v	$\alpha - 0^\circ$ 69.75%	$\alpha - 25^\circ$ $\alpha - 0^\circ$ 96%	$\alpha - 25^\circ$	$\alpha - \text{H}_2\text{O}$	$\alpha - 25^\circ$	$\alpha - \text{CH}_3\text{OH}$	$\alpha - 25^\circ$
31.5		0.900	0.875	0.309	0.830	-	$37.4^v$
44.67	0.981	0.937			0.916	-	75.47
43		0.913	0.934				
93.42	1.000	1.000			0.972	-	150.9
153		1.000	1.000				
352		1.000	1.000	0.934			

The values for conductivities in water are taken from Ostwald (op. cit.); those for methyl alcohol from Carrara (loc. cit.).

Where it is noted that the dissociation, as determined from the data, is greater in the 60.75% mixture than in water at the corresponding dilution. This is not the case for the 30% mixture.

What is also interesting is that, paradoxically, in both mixtures, the dissociation is greater at  $0^\circ$  than it is at  $25^\circ$ . Though the figures for the 69.75% mixture are not used to be relied upon this is true for the 90% mixture where the results are more reliable.



I have mentioned (p. 40) that the dissociation in the 20% mixture may be due to presence of the hydrate  $\text{Cu}_2\text{OH}_2\text{SO}_4$ . This hydrate would be more stable at a lower than at a higher temperature and would be present at the lower temperature to a greater extent, and being present to a greater extent, the dissociation would be greater. This should be the case for salts as well as for hydrochloric acid. Data, however, are not at hand for comparison. Lindsay's data for lithium nitrate are available and have been used (Table ). From this table apparently the dissociation is greater at the higher temperature. But, as I have said (p. 40), no certain conclusions are to be drawn from these data since we cannot be certain that limiting conductivity values were reached by Lindsay. In the case of hydrochloric acid, however, they were reached, in one instance, at least. Further investigation will be needed to decide this matter.

It is interesting at this point to see whether the hypothesis of Dutoit and Aston<sup>(1)</sup> is quantitatively true for the cases that have been considered. The hypothesis of Dutoit and Aston is that the dissociating power of a solvent is dependent upon its association (as determined by the Tammann and Shields<sup>(2)</sup> surface-tension method.) If the hypothesis held quantitatively it may be formulated

(1) J. C., 145, 240. (1920).

(2) J. Chem. Phys. 12, 433, (1944).





$$\frac{\alpha}{i'} = \frac{x}{x'}$$

where  $\alpha$  and  $\alpha'$  are the dissociation constants for the solutions compared,  $x$  and  $x'$ , the association factors of the solvents. The relation may be put into the form

$$\frac{\alpha}{x} = \text{const.}$$

In comparing solutions in different solvents, there should be the same number of gram-molecules of electrolyte dissolved in the same number of gram-molecules of each solvent. Where solutions in water, methyl alcohol and ethyl alcohol are to be compared the dilutions will be in the ratio 18 : 40 : 58 - approximately.

I have made a comparison on this basis, for potassium and sodium iodide in water, and methyl and ethyl alcohols. For the ethyl alcohol solution the dissociation was calculated from data of Böllmer<sup>(1)</sup>. The rest of the data were taken from the preceding tables.

(1) Zind. Ann. 51, 328, (1894).



Table 49.  $\chi$  for potassium and sodium iodides in water and methyl and ethyl alcohols.

	$H_2O$ $x = 3.68$	$CH_3OH$ $x = 3.43$	$C_2H_5OH$ $x = 3.74$	
	<i>const.</i>	<i>const.</i>	<i>const.</i>	
KI	34.9	25.3	24.9	
NaI	23.5	25.7	23.6	$v = 32, 04, 100$
	24.5	25.1		$v = 04, 125$
KBr	25.8	26.2		$v = 125, 130$

Similarly, assuming that Dutoit and Aston's hypothesis holds for 50%  $CH_3OH$ , we may calculate its degree of association. Taking the value of the constant as 23.6, and the compressibility volume for the mixture as 48, from the relation  $\frac{\chi}{x} = 23.6$  we may find  $x$ . We have  $\frac{93.7}{x} = 23.6$ , whence  $x$  equals 3.96.

A mixture of methyl alcohol and water containing 10% methyl alcohol by volume, has very approximately the composition corresponding to the hydrate  $CH_3OH \cdot 3H_2O$ . The existence of alcoholic hydrates has been explained on other grounds. Of this more will be said in another connection. It is possible that such hydrates, in virtue of their complexity have dissociative power. The greater dissociation found in 50% fifty percent mixture has been attributed to water being four simple molecules associated to form a central molecule. In water the molecules themselves are less than four.



Cause of the Maximum.

The first observers of the maximum, Zelinsky and others, offered no satisfactory explanation of it. They suggested that it might be connected with formation of hydrates of butyl alcohol. Farther than this they did not go.

Simsday (loc. cit.) offer the following explanation.

"According to the theory of Ostroff and Aston it is only those substances whose molecules are polymerized that can dissociate dissolved electrolytes. If this be true, it is probable, since those substances which dissociate dissolved electrolytes also show in general a normal molecular weight for dissolved non-electrolytes, that this breaking down of the polymerized molecule can be accomplished best by another associated molecule. From this it follows that the effect of mixing two associated solvents would be to lower the state of association of one or both until a state of equilibrium is reached. Such a mixture would be that of water and either ethyl or propyl alcohol, or a mixture of ethyl alcohol and propyl alcohol. In these cases since the molecules are first associated then the constituents, we would expect dissolved electrolytes to show a conductivity lower than that required by the law of mixtures. In every solvent with which I am acquainted this is exactly what has been



observed. In the mixtures of methyl alcohol and water, where the association of the constituents is the greatest, the lowering of conductivity is also the greatest, as would be expected.

In support of the above view that an associated solvent can diminish the association of another associated solvent, we have experimental evidence in the results of freezing-point measurement. The molecular weights of the alcohols in water, as determined by the freezing-point method, are normal, while the surface-tension method of Ramsay and Shields firmly beyond question, that the alcohols are associated compounds.

The effect of temperature on the lowering of the conductivity is in accord with the above suggestion. Since the effect of rise in temperature is to lower the extent of association of an associated liquid, it would be expected that at the higher temperature the influence of the alcohol on each other would be less than at the lower temperature. That this is the case can be seen by comparing the results at  $0^{\circ}$  with those at  $25^{\circ}$ .

The explanation of Lindsay was later strengthened by the investigation of Jones and Macrae<sup>(1)</sup>, who have made a study of the freezing points of solutions of acetic and formic acids

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(1) Amer. Jour. Chem. 30, 381, (1908).





and glycerol - formic acid in formic acid, formic acid in formic acid, acetic acid in water, etc. - that the conductivity in any solvent is diminished by the presence of another non-ionizing solvent.

According to the explanation of Lindsay, the whole effect is due to a diminution of dissociation and a consequent decrease in conductivity. I have shown that in the fifty percent mixture of methyl alcohol and water the dissociation instead of being diminished by the presence of the alcohol (or by bringing together water and the alcohol) is actually increased. This fact alone suffices to prove that the explanation offered by Lindsay cannot be correct.

Two factors determine conductivity - the amount of dissociation and ionic mobility. Decrease in one or both of these produces decrease in conductivity. I have shown that the decrease in conductivity in question cannot be due to decrease in dissociation. The inevitable conclusion is, then, that it is due to a decrease in ionic mobility.

A complete explanation of the minimum in conductivity will have to account for the following facts.

1. The effect itself.
2. The fact that the effect is more pronounced at a lower temperature than at 5 miller.



3. The fact that increasing of temperature (and in some cases increase of concentration) shifts the minimum toward a mixture containing a larger percent of alcohol.

There is a close connection between the viscosity or fluidity of a solvent and the conductivity of electrolytes dissolved in it as solvent. The greater the fluidity, or, the less the viscosity, other things being equal, the greater is the conductivity. This close connection is shown by the fact that for certain aqueous solutions the temperature coefficients of conductivity and of fluidity are identical. The connection between conductivity and fluidity, or viscosity, will be considered in detail in the concluding part of this dissertation.

The investigations of Lindsay, Zeigler and Krapivinsky of myself have been concerned with conductivities in mixtures of solvents. Numerous observations have been made on the viscosities of mixtures of liquids, notably by Arrhenius, (1) (2) Tagliani and Battelli (3) and Traube (4). All of these observers have found that in the case of mixtures of

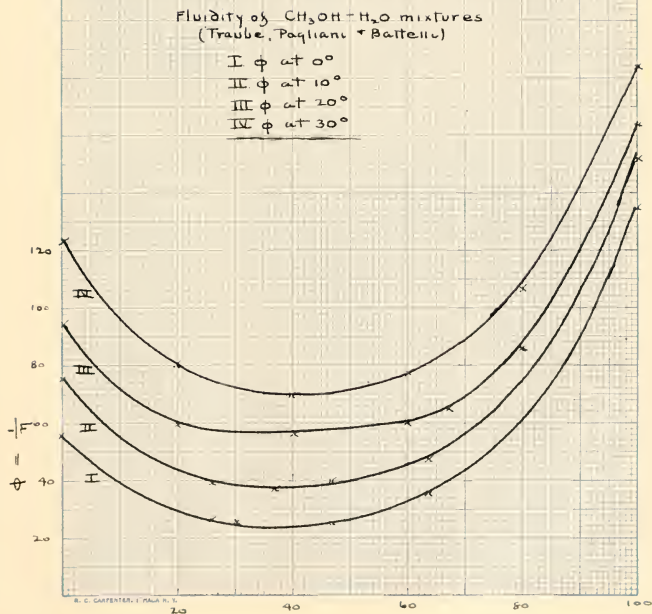
(1) Lieb. Ann., 123, 90, (1861).

(2) Wied. Abh. 37, 283, (1893).

(3) Atti di P. Acc. delle Sc. di Torino. 1A, 907 (1893).

(4) Ber. 10, 271, (1867).





Percent  $\text{CH}_3\text{OH}$  by weight

Fig. VI



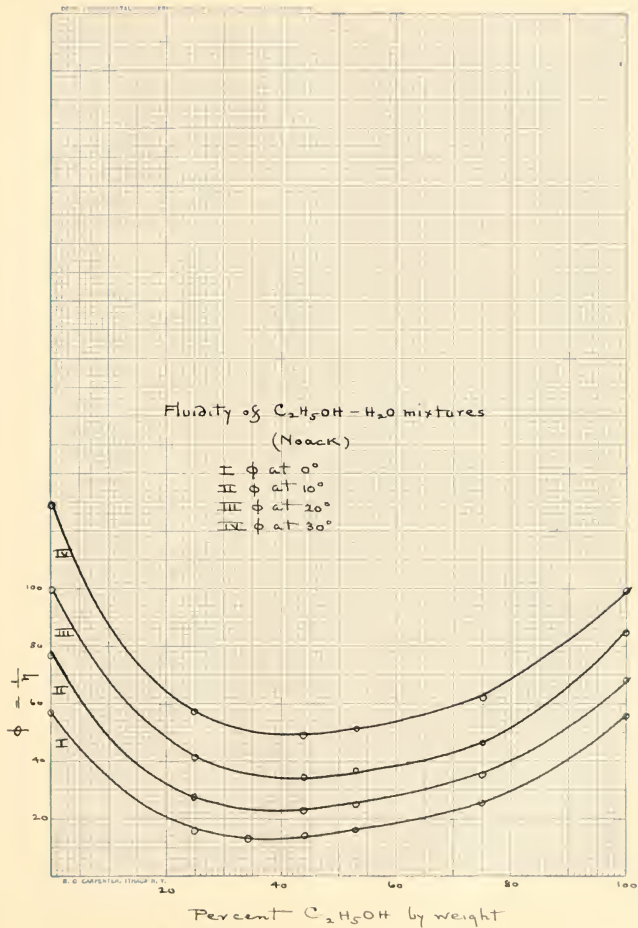


Fig VII





various mixtures and water, striking agreement is observed. In all cases the viscosity of the mixture is much greater than would be expected from the rule of averages. This is best shown graphically by plotting the viscosities as ordinates and the percentage composition of the mixture as abscissae. The viscosity curve is seen to pass through a maximum. The fluidity of a liquid is the reciprocal of its viscosity. If, therefore, we show graphically the variations in fluidity as the variations in viscosity were shown, the fluidity curve is seen to pass through a minimum. In all cases, of course, the fluidity is less than a proper average.

For the mixtures in which the minimum of conductivity is found to occur are approximately the mixtures in which the minimum of fluidity is found to occur. The explanation of the conductivity minimum that I offer is the following.

The minimum of conductivity is caused by the great decrease of fluidity resulting when the two components of the mixture are brought together.

For the results of Parlini and Battelli (loc. cit.) and of Traube (loc. cit.) I have calculated the various fluidities of mixtures of methyl and ethyl alcohol and water, for the temperatures 0°, 10°, 20°, and 30°, and have plotted the fluidity curves (figs. 4-7) in the manner indicated.



From a consideration of these curves it is evident that for mixtures of water and ethyl alcohol at 0° the minimum of fluidity occurs in a mixture containing 31%  $\text{C}_2\text{H}_5\text{OH}$  by weight (35% by volume) at 20 the minimum occurs in a 40% (46% by volume). Further, the drop in fluidity is more pronounced at the lower temperature.

For the mixtures of ethyl alcohol and water, at 0 the minimum occurs in a 34% (40% by volume) mixture. At 50 the minimum is found in a 50% (56%) mixture. The minimum is also more pronounced at the lower temperature.

It should be noted that the change in fluidity is very small over a considerable range - particularly in the case of mixtures of ethyl alcohol and water. At 50° the change of fluidity between 30 and 60% is very slight.

We have here fulfilled all the requirements of a complete explanation of the minimum. The two phenomena are parallel throughout; they are either causally connected or have some common cause. The former supposition is much more probable - particularly in the light of the proved connection between conductivity and fluidity.

The parallelism may be summed up as follows;



1. The conductivity minimum is found to be accompanied by a minimum in fluidity.
2. Both minima are more pronounced at lower temperatures, and both occur at approximately the same points.
3. The effect of increase of temperature is the same upon both minima - there is a shifting toward a mixture containing a greater percent of alcohol. However, the fluidity minimum, so to speak, lags behind the conductivity minimum.

For comparison the following tables are taken from Lindsay's work.

Table 30. Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 0°.

v	0%	20%	40%	50%	65%	80%	100%
64	74.09		35.48	35.73	35.12	39.03	59.52
128	76.47	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.53	67.73
512	78.05	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.36	49.07	37.85	36.76	37.75	44.45	71.55



Table 31. Comparison of the Molecular Conductivities of Strontium Iodide in Water, ethyl alcohol, and Mixtures of these Solvents at 25°.

v	0%	20%	40%	50%	65%	80%	100%
64	132.1	31.91	72.14	67.46	65.04	67.98	83.89
138	135.4	93.78	73.63	68.73	67.25	80.35	87.43
256	138.0	35.64	75.14	70.37	68.78	71.83	93.75
512	139.6	97.12	76.25	71.72	70.00	73.16	98.38
1024	140.7	98.10	77.68	72.57	70.94	74.81	102.0

It is seen that at 0° the minimum of conductivity occurs in a 10% mixture; the fluidity minimum occurs in a 40% mixture. At 25° the minima occur in 65 and 50% (for 30°) mixtures respectively.

Strontium Iodide also affords a good example of the shifting of the minimum, as the following tables from Lindsey's work show.

Table 32 Comparison of the Molecular Conductivity of Strontium Iodide in Water, Ethyl alcohol, and Mixtures of these solvents at 0°.

v	0%	35%	50%	75%	100%
32	113.1	63.00	50.13	35.33	7.82
64	117.7	67.05	51.61	35.24	85.01
128	118.1	68.62	53.03	33.83	94.76
256	122.0	70.98	57.17	36.67	106.4
512	124.1	83.36	59.37	69.73	114.0
1024	125.5	77.24	61.05	72.03	120.8





Table 33. Comparison of the Molecular Conductivity of Strontium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents at 25°.

v	0%	25%	50%	75%	100%
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.8	152.3	120.1	118.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	243.9	161.9	128.5	131.4	166.3

In the case of Strontium iodide the real minimum would probably be found in a mixture between the 50 and 75% mixtures.

So, also, in the case of lithium nitrate, as shown in the tables following taken from Lindeay.

Table 34. Comparison of the Molecular Conductivity of Lithium Nitrate in Methyl Alcohol, Water, and Mixtures of these Solvents at 0°.

v	0%	25%	50%	75%	100%
32	50.00	29.15	23.59	26.67	45.99
64	51.49	29.88	24.49	27.35	50.11
128	52.11	30.11	25.03	27.66	53.95
256	53.42	30.70	25.71	28.31	56.67
512	54.76	31.35	26.35	29.61	60.76
1024	55.10	32.24	27.35	31.91	65.40



Table 22. Compositions of the molecular weight (v) of 1,1,1-trichloro-2-methyl-2-propyl alcohol, ether, and mixtures of these solvents at 23°.

v	0%	25%	50%	75%	100%
32	91.83	60.56	47.89	47.00	63.51
64	94.62	62.16	49.92	49.32	65.32
128	95.00	63.77	51.00	51.04	71.51
256	99.28	64.96	53.57	54.36	80.57
512	101.3	66.72	54.02	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

Upon examining my own values for sodium iodide (p19) it is seen that at 0 the minimum occurs in the 50% mixture. At 32 for one dilution  $v = 32$ , it occurs in the 75% mixture, elsewhere in the 50% mixture. In all probability the real minimum would be found in an intermediate mixture.

When we attempt a comparison for ethyl alcohol the data are more meagre. The minimum was found by Lindsay to occur at 0° only in the cases studied by him. I give his data.



Table 56. Comparison of the Molecular Conductivity of sodium acetate in water, ethyl alcohol and a 50 percent mixture of these solvents at 0°.

v	Water	Mixture	Ethyl Alcohol.
	0°	0°	0°
4	74.22	19.42	10.71
128	75.23	19.89	10.55
256	76.62	20.03	10.60
512	77.49	20.70	10.60
1024	77.78	21.50	10.58

Table 57. Comparison of the Molecular Conductivity of Potassium Iodide in Ethyl Alcohol, water, and a 50 percent mixture of these solvents at 0°.

v	Water	Mixture	Ethyl Alcohol.
	0°	0°	0°
64	74.09	19.26	10.12
128	76.4	19.81	10.36
256	77.01	20.35	10.60
512	78.0	20.94	10.60
1024	77.96	21.45	10.45



Table 23. Viscosities of solutions of calcium acetate in water at 0°.

v	H <sub>2</sub> O	50% CaH <sub>3</sub> O <sub>2</sub>	CaH <sub>3</sub> O <sub>2</sub>
12	50.0	13.10	14.22
64	51.49	13.56	15.00
128	52.51	14.27	17.11
256	53.40	14.63	19.39
512	54.70	15.45	1.38
1024	55.30	16.23	23.29

Examination of these data shows that the viscosity minimum occurs in a 50% mixture. The fluidity minimum occurs in a 40% mixture. However, the conductivity minimum might well occur at some other point, and consequently it is hardly safe to press the matter too far.

Lindsay also made some measurements in mixtures of methyl and ethyl alcohols. No minimum was observed, the conductivities found being about what would be expected from the rule of averages. This is clearly due to the fact that when these two solvents are brought together they do not exhibit the same phenomenon as in a 50% in the case of mixtures of alcohols and water. I can find no data relative to the fluidity of mixtures of methyl and ethyl alcohols. Arrhenius<sup>(1)</sup>

(1) Ztschr. f. phys. Chem., 1, 117, (1897).





states, however, that there is no striking change when the two are brought together.

The best method, however, of comparing the variation in conductivity and in fluidity is not in the discussion of the conductivity and fluidity curves. This method can only be approximate. It is best to compare the respective rates of decrease (by percent) of the two - that is the differences in percent from what would be expected from the rule of averages. These average values may be found graphically as follows. At the extremities of a straight line of chosen length erect perpendiculars proportional in length to the respective conductivities (or fluidities) in the two components of the mixtures and connect these by a straight line. Divide the base line into parts proportional to the composition of the various mixtures. The perpendiculars joining these points of division and the line previously drawn will be proportional in length to the various average conductivities (or fluidities). This can best be done by the use of coordinate paper. The foregoing method has been used in making the following comparisons.

Table 33. Variation ( $\Delta\mu$ ) in conductivity (Percentage fall in conductivity) of potassium iodide in mixtures with 1



alcohol and water - 45.25° (1).

v	20°	40°	60°	80°	100°	solids
100	0.329	0.425	0.413	0.309		
101	0.334	0.412	0.450	0.313		
113	0.340	0.481	0.473	0.336		
1034	0.339	0.483	0.464	0.344		
1045	0.340	0.485	0.464	0.343		
Variation in Fluid- ity - $\Delta\phi$	0.401	0.827	0.601	0.466		

It is seen that the variation in fluidity is in all cases greater than the variation in conductivity. The two variations must be compared in order to see where the effect of variation is greatest. If the two effects were exactly equal  $\frac{\Delta\phi - \Delta\mu}{\Delta\phi}$  would equal zero. In this relation we have means of comparing the two effects. I have made the comparison in the following table.

(1). The conductivity data were taken from the work of Tolman (loc. cit.).



Table 66. Comparison of variations in conductivity and in fluidity. —  $\frac{\Delta\phi - \Delta\mu}{\Delta\mu}$

v	10%	20%	30%	40%	50% 60% 70% 80% 90%
133	0.367	0.350	0.273	0.339	
336	0.382	0.378	0.350	0.333	
512	0.239	0.231	0.231	0.283	
1024	0.239	0.231	0.232	0.262	
2048	0.239	0.231	0.232	0.262	

It is evident that the effect of variation of fluidity on conductivity is greatest in the 40% mixture, for pure the values of the quotients are least. It is seen that the effect decreases with increasing dilution and finally becomes constant.

I give similar comparisons for potassium iodide in mixtures of methyl alcohol and water at 0° and at 2°, using Lippman's results.



Table 22. Variation (percentage Table 10) in conductivity of solution due to mixture of tetra alcohol and water at 25°C and at 0° -  $\Delta\mu$ .

v	20%	40%	50%	60%	80%	100% $\text{C}_2\text{H}_5\text{OH}$
64 - 0°		0.179	0.194	0.150		
128 - 25°	0.237	0.354	0.372	0.350	0.327	
128 - 0°	0.361	0.507	0.510	0.478		
156 - 25°	0.257	0.368	0.386	0.360	0.265	
156 - 0°	0.308	0.509	0.502	0.486		
212 - 25°	0.262	0.377	0.394	0.371	0.300	
212 - 0°	0.304	0.510	0.513	0.469		
264 - 25°	0.262	0.379	0.399	0.381	0.313	
264 - 0°	0.361	0.503	0.508	0.490		
$\Delta\phi - 0^\circ$	0.302	0.393	0.404	0.386	0.310	
$\Delta\phi - 25^\circ$	0.543	0.695	0.695	0.682		
			0.575			

Table 23. Comparison of variation in fluidity and in conductivity  $\Delta\phi - \Delta\mu$ .

v	30%	40%	50%	65%	80%	100% $\text{C}_2\text{H}_5\text{OH}$
64 - 0°		0.311	0.333	0.351		
128 - 25°	0.354	0.303	0.304	0.332	0.312	
128 - 0°	0.335	0.275	0.266	0.293		
156 - 25°	0.300	0.289	0.296	0.301	0.314	
156 - 0°	0.332	0.268	0.261	0.280	0.309	
212 - 25°	0.319	0.266	0.263	0.283		
212 - 0°	0.276	0.264	0.252	0.281	0.278	
264 - 0°	0.312	0.270	0.260	0.280		
264 - 25°	0.290	0.263	0.26	0.291	0.280	





In the following comparison is made for lithium nitrate.  
 Table 63. Variation (Percentage fall) in conductivity of  
 lithium nitrate in mixtures of ethyl alcohol and water.  
 0° and 25°. (From Lindsay's data.)

	25%	50%	75%	CH <sub>3</sub> OH by volume.
32 - 0	0.406	0.508	0.432	
25	0.285	0.354	0.333	
64 - 0	0.417	0.518	0.443	
25	0.296	0.392	0.345	
128 - 0	0.432	0.532	0.466	
25	0.307	0.405	0.358	
256 - 0	0.436	0.535	0.472	
25	0.314	0.400	0.362	
512 - 0	0.441	0.541	0.477	
25	0.310	0.408	0.354	
1024 - 0	0.434	0.541	0.477	
25	0.300	0.411	0.354	
- 0	0.600	0.695	0.661	
25	0.450	0.475	0.481	



Table 64. Coefficient of variation in conductivity and fluidity.  $\frac{\Delta\phi - \Delta\mu}{\Delta\phi}$  at 0° and at 25°.

v	25%	50%	75%	CH <sub>3</sub> OH by volume.
32 - 0°	0.323	0.309	0.318	
25°	0.375	0.332	0.308	
64 - 0°	0.305	0.255	0.330	
25°	0.351	0.318	0.283	
128 - 0°	0.280	0.235	0.294	
25°	0.327	0.300	(0.255)	
256 - 0°	0.273	0.230	0.244	
25°	0.311	0.294	(0.247)	
512 - 0°	0.265	0.222	0.277	
25°	0.318	0.290	0.264	
1024 - 0°	0.277	0.222	0.277	
25°	(0.344)	0.285	0.264	

In the following tables are given the data for sodium iodide, using my own results.

Table 65. Variation (Percentage fall) in conductivity of sodium iodide in mixtures of methyl alcohol and water at 0° and at 25°.

v	25%	50%	75%
32 - 0°	0.400	0.485	0.411
25°	0.277	0.357	0.298
64 - 0°	0.406	0.500	0.419
25°	0.283	0.378	0.310
128 - 0°	0.409	0.511	0.423
25°	0.297	0.393	0.318
256 - 0°	0.408	0.508	0.433
25°	0.313	0.395	0.350
512 - 0°	0.409	0.500	0.440
25°	0.321	0.402	0.333



Table 66. Comparison of variations in fluidity and in conductivity.

v	25%	50%	75%.
32 - 0	0.333	0.302	0.378
25	0.392	0.379	0.364
64 - 0	0.313	0.273	0.366
25	0.379	0.315	0.355
128 - 0	0.320	0.260	0.360
25	0.318	0.312	0.339
256 - 0	0.320	0.269	0.345
25	0.313	0.313	0.314
512 - 0	0.310	0.281	0.325
25	0.296	0.301	0.308

Finally I give a comparison of the temperature coefficients of conductivity for various electrolytes and for the various mixtures.

Table 67. Comparison of temperature coefficients of conductivity and of fluidity for various electrolyte in  $\text{CH}_3\text{OH}$  -  $\text{H}_2\text{O}$  mixtures.

	25%	40%	50%	65%	75%	100%
$\phi = 0$	30.6	27.0	27.8	34.5	39.75	131.3-3.8
$\phi = 35$	59.04	63.4	60.65	68.9	81.85	183.1 22.4
$\frac{1}{\phi} \frac{\Delta \phi}{\Delta t}$	0.0213	0.0230	0.0216	0.0200	0.0205	0.0125
$\frac{1}{\phi} \frac{\Delta \mu}{\Delta t}$						
$\frac{1}{\mu_{25\%}} \frac{\Delta \mu}{\Delta t}$		0.020	0.0187	0.0187		0.0121
$\text{NaI}$	0.0202		0.0202		0.0179	0.0147
$\text{LiNO}_3$	0.0211		0.0203		0.0155	0.0112
$\text{SrI}_2$	0.0213		0.0210		0.0177	0.0152
$\text{CaI}_2$	0.0238		0.0220		0.0173	

The velocities were 1025 for  $\text{KI}$ , 1100,  $\text{SrI}_2$ , 256 for  $\text{NaI}$ , 110 for  $\text{CaI}_2$ .



The temperature coefficients are seen to be most nearly equal in the four mixtures for all four binary salts in the 50%.

Table 18. Comparison of temperature coefficients of conductivity and fluidity for various electrolytes in  $\text{C}_2\text{H}_5\text{OH} - \text{H}_2\text{O}$  mixtures.

	0%	40%	50%	75%	100%
$\phi = 0^\circ$	55.39	42.8	14.15	25.6	55.5
$\phi = 35^\circ$	112.00	60.7	41.75	55.1	85.0
$\frac{1}{\phi_{25}} \frac{\Delta\phi}{\Delta t}$	0.0249	0.0250	0.0264	0.0210	0.0142
					(Noack)
$\frac{1}{\mu_{25}} \frac{\Delta\mu}{\Delta t}$					
KI	0.0172		0.0237		0.0135
$v = 1024$					
$\text{LiNO}_3$	0.0184		0.0251		0.0138
$v = 1024$					
$\text{ErI}$	0.0272		0.0247		0.0199
$v = 1024$					
$\text{Ca}(\text{NO}_3)_2$	0.0182	0.0233	0.0245	0.0210	0.0131

It is evident from the data that for the four salts KI,  $\text{LiNO}_3$ ,  $\text{ErI}$ , and  $\text{Ca}(\text{NO}_3)_2$ , the quotient  $\frac{\mu}{\phi}$  is constant to within 10% (5% for  $\text{LiNO}_3$ ).

For the binary salts, 490 for  $\text{Ca}(\text{NO}_3)_2$  this holds for the pure solvent,  $\text{C}_2\text{H}_5\text{OH}$  also, even more closely.





### Interpretation of Results.

The value of the quotient  $\frac{\Delta\phi}{\Delta\mu}$ , is a measure of the parallelism between the two phenomena, decrease in conductivity and decrease in fluidity. If the decrease were the same in both cases, other conditions being the same, the value of the quotient would be zero. The fact that it is not zero indicates that the decrease in ionic mobility resulting from the decrease in fluidity is not proportional to this latter decrease.

When we come to compare the effect in the case of potassium iodide in mixtures of the two alcohols and later (Tables 55 and 57), it is seen that the effect of decrease in fluidity on ionic mobility is greatest in the ethyl alcohol mixtures, or the two effects are here most nearly parallel. The effect is less for potassium iodide in methyl alcohol mixtures at both temperatures of observation 0° and 25°. It is to be remembered that we are leaving out of account possible differences of dissociation. Increase of dissociation in the mixture over that of the aqueous solution corresponding would subtract from the effect of decrease in fluidity. Apparently this possible increase in dissociation cannot be very great, as some of my measurements show - not more than one or two percent. A far smaller and easily compensable error in dissociation would be necessary to account



for the difference in the two effects.

Now, the minimum is much more pronounced in the case of alcohol mixtures, occurring in the methyl alcohol mixtures generally at  $0^{\circ}$  and not being very marked. We have just seen that the real effect is greater in the latter case, when we make a proper comparison. The conclusion is, then, that the minimum in conductivity is so to speak, merely incidental. The reason why it is not so marked in the case of the ethyl alcohol mixtures is to be found in the small conductivities in ethyl alcohol, these, in turn, as will be shown in the last part of this dissertation, being small on account of the relatively great viscosity of ethyl alcohol, and its rather small dissociating power. On the other hand, the phenomenon does exhibit itself in the other mixtures, and it is because of the high conductivities in methyl alcohol; these being high on account of the small viscosity of methyl alcohol and its relatively great dissociating power.

Considering all the salts in the various mixtures, it is seen that, in general, the effect of increase viscosity on conductivity is greatest in that mixture in which the minimum in conductivity occurs. In some cases the maximum effect occurs elsewhere. For example, for lithium nitrate (Table 50) at  $25^{\circ}$  the maximum effect is in the 7% mixture, while the minimum in conductivity occurs for the next part of the 35% mixture.



The explanation of this is to be found in the fact that, although in the one mixture the effect is greater, this greater effect is offset by the effect of the smaller fluidity of the other mixture, that of the 75% mixture being 61.8, and that of the 50% mixture being only 68.9 . In cases where the minimum shifts with increase of dilution, the probable explanation is to be found in the increase of dissociation accompanying further dilution.

The effect of variation in temperature is also shown in the tables - particularly in the case of lithium <sup>nitrate</sup> (Table 60). At 0 the maximum effect is in the 50% mixture, at 25° , in the 75% mixture.

In the last two tables (63 and 64) is given a comparison of the temperature coefficients of fluidity and of conductivity for various electrolytes in the various mixtures of methyl alcohol and water, and also for ethyl alcohol mixtures, for which the data are more meagre.

From table 63 it is evident that the temperature coefficients of conductivity and fluidity do not differ markedly, particularly for weak salts. For dissolving double salts the two are nearly equal in the 50% mixture, differing by only seven percent. For the other salts in the 50% mixture the difference is slight, and in dilution and in low temperatures the



for rotation is also in the same mixture. In some instances the agreement is even to be much closer. (see I and II).

For the ethyl alcohol mixture, 50%, the temperature coefficients are seen to differ to about the same degree as in the methyl alcohol mixtures. In other words,  $\frac{\Delta \kappa}{\Delta T} = \text{const.}$

These facts are significant, as will appear from the last part of this dissertation.

My conclusion is, then, that the fall in conductivity of electrolytes in binary mixtures of various alcohols and water, which is in some cases accompanied by the minimum conductivity, observed by Zelinsky and Prapiwin, is caused by a diminution in the fluidity of the solvent, and a consequent decrease in ionic mobility.





### VISCOSITY AND CONDUCTIVITY.

The viscosity of a liquid or solution is defined as being the force (in dynes) necessary to move a layer of the liquid or solution one molecule in thickness and of unit area (1 sq. cm.) over another layer of the liquid with the unit velocity (1 cm. per sec.). The symbol  $\eta$  is used for the coefficient of viscosity. The fluidity of a liquid is the reciprocal of its viscosity -  $\phi = \frac{1}{\eta}$ .

Two methods have been used in the determination of viscosity - that of Coulomb, in which the coefficient is calculated from observations of the damping of the oscillation of a solid oscillating in the liquid, and that of Poiseuille, which derives the constant from observation of the rate of flow of the liquid through a capillary tube.

That there is a connection between the viscosity of a solvent and the electrical resistance of solutions of electrolytes in the solvent has long been known. Or, what amounts to the same thing, there is a parallelism between fluidity and conductivity.

There have been a number of investigations concerning this relation. The earliest is that of Wiedemann<sup>(1)</sup>. Wiedemann's (1). Ann. Chem. Phys. 33, 249, 1827.



method of varying the fluidity of the solution was by varying the concentration. From his study of copper sulphate solutions of different concentrations, Wiesemann concluded that conductivity is directly proportional to the viscosity of the solution. That is  $\frac{K\eta}{c} = \text{const.}$  where  $K$  is the conductivity,  $\eta$ , the coefficient of viscosity,  $c$ , the concentration of the solution in parts by weight of electrolyte to one hundred parts of solvent.

(1)

Grottrian<sup>(1)</sup>, in his investigation, used a second method of varying fluidity, that is, by varying the temperature. A comparison was made between the temperature coefficients of fluidity and of conductivity. Grottrian found that in many cases the two coefficients are approximately the same. Wiesemann and Grottrian had worked with solutions of rather high concentration. Thinking that less irregularities should be exhibited

(2)

by dilute solutions, Stephan<sup>(2)</sup> made a study of the conductivities of dilute solutions, containing not more than five percent, of sodium, potassium and lithium chlorides, and of sodium and potassium iodides in mixtures of ethyl alcohol and water. Stephan thus used the third possible method of varying fluidity - that of varying the solvent. Mixtures of alcohol and water were used because of certain striking phenomena

(1) . Berl. Ann., 119, 220, (1876).

(2) . Berl. Ann. 17, 473, (1863).



exhibited by these mixtures. When alcohol is added to water there is remarkable increase in viscosity over and above what would be expected from the rule of mixtures. Shown graphically by plotting the composition of various mixtures as ordinates and the viscosity of the mixtures as abscissae, the viscosity curve is seen to pass through a maximum. These facts have been illustrated and more fully treated in the first part of this dissertation (p. 49). Stephan also studied the effect of temperature upon the conductivities and fluidities involved, and found, as had Grotrian (loc. cit.) in other cases, that the temperature coefficients of both are approximately equal.

Stephan sought to establish the relations

$$k = \frac{KH}{\eta} \quad \text{and} \quad k = \frac{w}{w'} \cdot \frac{KH}{\eta}$$

the first holding for all mixtures up to the mixture of minimal fluidity, and the second from this point on.  $K$  in both formulae is the conductivity of the equivalent solution of the salt,  $k$  is its conductivity in the mixture,  $H$  and  $\eta$  are the viscosity coefficients for water and for the mixture respectively. In the second relation,  $w$  is the percent of water in the mixture, and  $w'$  the percent of water in the aqueous alcoholic mixture of minimal fluidity. Stephan's conclusion is that ionic friction is either proportional to or equal to internal friction (vis-



viscosity). That each ion carries with it two or three molecules of solvent, and that the ionic friction depends on frictions between these and the rest of the solvent.

The agreement with these formulae was not very close, particularly in the case of the second. Why this is so has not readily to be seen. Stephan has not taken into account one important factor in conductivity - dissociation. Certainly with various mixtures there would be varying degrees of dissociation.

(1)

Grossmann made use of the data furnished by Grotrian (loc. cit.). Grotrian's determinations of viscosity were made by the method of Coulomb. By the aid of a new formula, devised by himself, Grossmann recalculated Grotrian's results, and concluded that the product of the viscosity and the conductivity of a solution is constant, and independent of the temperature. This constancy is shown by the fact that the temperature coefficients of conductivity and of viscosity (as calculated by his method) are the same to within less than one percent, in most cases to within less than one-half of one percent. This he showed to be true for solutions of the chlorides of potassium, sodium, calcium and magnesium, and of zinc sulphate.

(1). Wied. Ann. 18, 119, (1883).





were the only difficulty is in the solvent used. The reliability of this must be granted, and it is questionable whether this can be done.

(1)  
Arrhenius in the investigation already referred to (p. 3) on the effect of the addition of small quantities of nonelectrolytes on the conductivity of aqueous solutions found an empirical relation between the conductivity of the solution and the viscosity of the solvent. The equation is

$$1000 \kappa = c + 1000 c' (\eta - 1)$$

where  $c$  and  $c'$  are constants for the given solvent,  $\eta$  is the viscosity of a one percent aqueous solution of the nonelectrolyte (that of water being taken as unity) and  $\kappa$  is the coefficient  $\kappa$  in the equation,  $\lambda = \lambda_0 (1 + \frac{\kappa}{2x})$ , the meaning of which has already been explained (p. ).

(2)  
Holland worked in the same field as did Arrhenius. He found the relations of Stephan already cited inapplicable to the cases studied by him, and also that of Arrhenius just given. Holland concludes that though there is a connection between conductivity and viscosity, it is unknown.

(3)  
Strandberg merely repeated and confirmed some of the work of Arrhenius (loc. cit.).

(4)  
Föllner, in an admirable investigation on the conduct-

(1). Itscor. Phys. Chem., 9, 467, (1892).

(2). Wied. Ann. 50, 391, (1892).

(3). Itscor. Phys. Chem. 14, 221, (1894).

(4). Wied. Ann. 32, 326, (1892).



activities of various salts in methyl and ethyl alcohol, took occasion to determine the temperature coefficients of conductivity of the solutions studied, and found that these differed very little from the temperature coefficients of viscosity of the solvents, particularly for solutions in ethyl alcohol. For example,  $\Delta\mu$ , the temperature coefficient of conductivity - the mean for seven salts in ethyl alcohol solution - was 1.54 percent,  $\Delta\eta$  was 1.78% . Similarly  $\Delta\mu$  - the mean for six salts in methyl alcohol solution - was 1.3 percent,  $\Delta\eta$  for methyl alcohol was 1.45 . In every case, at high dilutions, there was found to be a parallelism between the two temperature coefficients.

(1)

(2)

Euler extending the work of Arrhenius on the viscosity of mixtures, finds a connection between viscosity and ionic mobility. Arrhenius had proposed exponential formula

$$\eta(x, y) = A e^{Bx} \text{ or } \eta_s = A^s$$

where  $\eta$  is the viscosity of the mixture, A and B are characteristic constants, x, the volume percent of the first component, and y, the volume percent of the second. In the second formula, which is another way of stating the first,  $\eta_s$  is the viscosity coefficient of a normal solution of the second component in

(1). Ztschr. Phys. Chem. 25, 530, (1908).

(2). Ztschr. Phys. Chem. 1, 285, (1887).



the first as solvent,  $x$ , the volume percent. Fikler extends the formula to partially dissociated electrolytes in solution, giving it the form

$$\eta = S^* A^x K^y$$

assigning a part of the viscosity to each component,  $S^*$  being that for the undissociated portion of the electrolyte,  $A$  and  $K$ , that for anion and cation respectively,  $x$  and  $y$  the concentrations, for normal solutions where the dissociation factor,  $\alpha$ , is known. The formula becomes

$$\eta = S^* (1 - \alpha)^{\frac{1}{2}} A^{\frac{1}{2}} K^{\frac{1}{2}}$$

Assuming that ions of the same mobility have the same viscosity constant, the constants for various ions may be determined.  $S^*$  may be found by determining  $\eta$  for two different concentrations of the same salt, of known dissociation, or the aid of the Arrhenius formula. When the viscosity coefficients for the various (univalent) ions are thus calculated and are plotted against the corresponding ionic mobilities, the corresponding points are seen to lie on a curve which may be expressed by the equation  $((K) - 0.68) \left( \frac{\eta}{U} \right) = \text{const.}$  where  $A$  and  $K$  are the viscosity coefficients,  $U$  and  $V$ , the ionic mobilities. The 1894  $\eta$  and  $UV$  do not satisfy the relation. This is later explained by reference to the viscosity proposed as the measure of electrostatic dissipation (1).

(1). *Trans. Roy. Soc. Lond.*, 1894, 1124.



(1) Massoulier<sup>1</sup> studied the conductivity of copper sulphate in aqueous solution of glycerol, and showed that as the viscosity increases with further addition of glycerol, the resistance of the solution increases proportionately.

(2) Kohlrausch<sup>2</sup> discusses a hypothesis advanced by him formerly before<sup>(3)</sup> which puts into more definite form ideas previously<sup>(4)</sup> and somewhat generally held. Kohlrausch had shown that

in the case of monovalent ions the temperature coefficient of ionic mobility is a function of the ionic mobility itself, just as Buller (loc. cit.) showed the ionic viscosity coefficient to be a function of ionic mobility. The exceptions are the same in both cases -  $H^+$  and  $OH^-$ . In the last article mentioned Kohlrausch points out that if we plot the conductivity curves of various electrolytes in a way to show the variation of conductivity with temperature, and in like manner show the variation of the fluidity of water with change in temperature, all these curves cut the zero axis at about the same point. That is, conductivity and fluidity disappear at the same point. Of course a wide extrapolation is necessary, and this fact must be taken into account. What is

(1). O. P. 130, 873, 1905.

(2). Ann. P. F., 71, 338, (1905).

(3). Sitz. Ber. Berliner Akad. 1901, 1025.

(4). Sitz. Ber. Berliner Akad. 1902, 874.





are significant, the conductivity curve for certain salts, notably sodium valerate, is almost identical with the fluidity curve. Further, for certain slow moving ions, Li for example, the temperature coefficient of ionic mobility is almost the same as that of fluidity.

In order to explain these facts and to avoid the tacit assumption that ionic motion is independent of motion of the solvent, Pohlrausch proposes the hypothesis that "about every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion" - - - "The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater dimensions".

This hypothesis accounts for the facts given before - the apparent disappearance of fluidity and conductivity at the same temperature, the coincidence in certain cases of conductivity curve and fluidity curve, and the equality of temperature coefficients of ionic mobility and of fluidity, and the fact that the temperature coefficient of ionic mobility is a function of the mobility itself. As stated, the conception of such ionic hydration is not new. The older work of Steiner (loc. cit.) advanced a similar view, likewise (1) (1) Grahmann and Bernst and others attributed to diffusion

(1). Steiner. *Phys. Chem.* 1, 182, 1889.  
(1). *Zeit. Chem.*



But due to the above two constant of this operation, is now some of certain derivative ions, and gave us the conclusion that it must be  $\text{H}_2\text{SO}_4$ . Euler<sup>(1)</sup> sees in dissociation a close union of ion and solvent - that is an ionic hydration.

The hypothesis of Kohlrausch is proposed for binary electrolytes, at high dilutions, and when water as a solvent. Its application is therefore restricted.

A more general hypothesis, applicable to a series of solvents and to various dilutions will have to take into account the following factors; first, the viscosity (or fluidity) of the solvent; second, the amount of dissociation in the solution; third, the dissociating power of the solvent. We shall have to find some relation between the dissociating power of the solvent and some constant property of the solvent.

There have been various hypotheses accounting for dissociating power. Verwey<sup>(2)</sup> finds a connection between dissociating power and the dielectric constant of the solvent. The same relation had been previously pointed out by J. J. Thomson<sup>(3)</sup>. In general, the higher the dielectric constant of a liquid, the greater is its dissociating power. Thomson /loc.

(1). *Wied. Ann.* 43, 173, (1897.)

(2). *Verh. d. Phys. Ges.* 13, 131, (1899).

(3). *Phil. Mag.* 32, 320, (1891).



nit.) shows on theoretical grounds what we would expect this to be true.

(1)

Bruhl<sup>1</sup>, finds in a condition of unsaturation the cause of tendency to polymerization, and of dissociating power. He holds the view that oxygen is usually quadrivalent and that water and the alcohols, for example, containing quadrivalent oxygen, are unsaturated compounds. Whence their tendency to polymerization and power to dissociate.

(2)

The hypothesis of Deitoe and Astor<sup>2</sup> has already been referred to in another connection, and has been shown to hold quantitatively in certain cases for water, methyl and ethyl alcohols. We have seen (p.44) that for solutions of various salts in these solvents the concept of dissociation (as determined from conductivity) is directly proportional to the dissociation factor of the solvent. We have seen, further, that the hypothesis does not apply in the case of acetic acid solutions. Nor does it for solutions in acetone.

It is plain that the hypothesis of Deitoe and Astor does not so very closely state the proposition - all that it indicates is that there is a parallelism between the amount of dissociation

(1). Ztschr. Phys. Chem. 10, 114, (1885).

(2). C. P. 121, 210, (1897).



ization and the extent of polymerization. The tendency seems to indicate association. The association may arise from the fact that the two properties - degree of dissociation and degree of polymerization are functions of some other property of the solvent. The Thompson-Cornell hypothesis (loc. cit.) is the only one that offers an explanation of deeper significance.

## (1)

Dutoit and Friedlander make an attempt to find a connection between conductivity, viscosity and association, and thus make a step in the direction of a more general hypothesis. From a study of conductivities of solutions of different electrolytes in different solvents they come to the following conclusion.

"The values of  $\mu_{\infty}$  for the same electrolyte dissolved in different solvents are a direct function of the degree of polymerization of the solvents, and an indirect function of the coefficient of viscosity of these solvents". That is,  $\mu_{\infty} = \text{const.} \cdot x$  where  $x$  is the association factor and the other symbols have the usual significance. The relation was found to hold only in a very general way - verified merely qualitatively.

When we come to consider the proposed relation it is





difficult to see how it could exist; that is, it is wholly empirical. It is not in accord with the hypothesis of Dulait and Aston. For when complete dissociation is reached the polymerization of the solvent is no longer an inflexible factor. It is useless to discuss the matter further at the moment, as stated, the relation  $\eta/\kappa$  holds quantitatively.

This will suffice to indicate what has to us for years endeavored to show a connection between conductivity and viscosity. The relations thus far brought to light are qualitative. Of far more importance is the establishment of a quantitative relation. I shall proceed to show that such a relationship does exist, and I propose the following hypothesis as to this relationship.

The conductivities of comparable, equivalent solutions of binary electrolytes in certain solvents (methyl and ethyl alcohols, other alcohols of the same series, acetone, etc.) are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent. To make the hypothesis of Dulait and Aston less objectionable for the solvent in question, the "association factor of the solvent" must be substituted "degree of dissociation of the solution".



formulated, the comparison is expressed by two relations

$$\frac{\mu\eta}{x} = \text{const. or, } \frac{\mu\eta}{\pi} = \text{const.}$$

where the symbols have the usual significance.

This becomes, when  $\pi =$

$$= \text{const.}$$

The product of  $\pi$  and the coefficient of viscosity is a constant for the same electrolyte in different solvents. Therefore use for  $x$ ,  $\pi$ , the constant is the same throughout.

The meaning of the term "equivalent comparable solution" will need to be defined. In comparing aqueous solutions it is evident that solutions of the same normality (containing equal gram molecules of electrolyte in equal volumes) are strictly comparable. It is evident that this is not the case when, for example, we come to compare solutions of the same electrolyte in different solvents. In order to be strictly comparable the solution must contain the same number of gram molecules of electrolyte dissolved in the same number of gram molecules of two different solvents, or equal weights of the (same) electrolyte dissolves in volumes of the compared solvents proportional to the molecular volumes of the solvents in question. This the only proper basis of comparison, has been indicated before (p. 43).



Comparison of variation in Conductivity  
in  $C_2H_5OH$  and in Fluidity of  $C_2H_5OH$ .

I. KI in  $C_2H_5OH$ ,  $v = 256$

II.  $LiNO_3$  " "  $v = 256$

III.  $NaCl$  " "

IV.  $LiCl$  " "

IV Fluidity Curve.

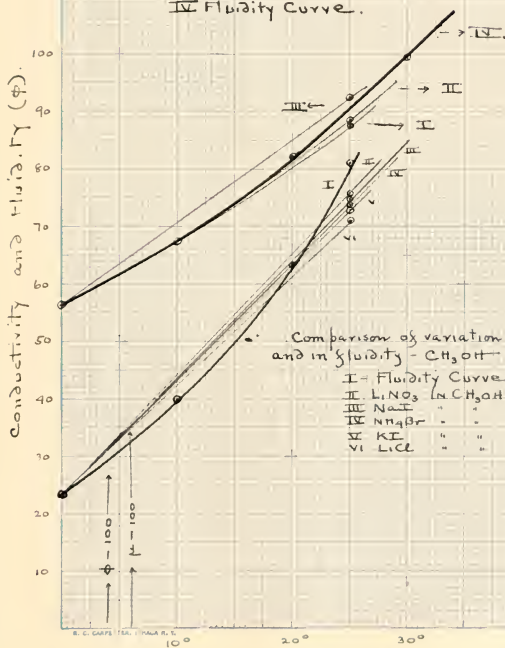


Fig. 411



to illustrate comparable solubilities in water, and in methyl alcohol, would be those containing 200 mole percent of electrolyte dissolved in 18 volumes of water and 40 volumes of methyl alcohol, for the molecular volume of water is eighteen, and that of methyl alcohol, approximately 40. The values compared should always be in the ratio 18 (of water) to 40 (of methyl alcohol). Similarly, in the case of methyl and ethyl alcohols, the ratio would be 40 to 57.5.

I shall now proceed to show that the Arrhenius holds good. In the first place I have plotted (Fig. VII) the variation of the fluidity of methyl and ethyl alcohols with temperature, taking the different fluidities ordinates, and the different temperatures abscissae. Plotted with these for comparison are the conductivities of various binary electrolytes in solution in the two solvents. Since only two observations were made in this case, one at  $0^{\circ}$  and the other at  $25^{\circ}$ , the variation in conductivity is shown by a straight line. If observations at intermediate points could be had this would probably not be the case - the line would be a curve. The first ordinate - that at  $0^{\circ}$  - is made the same in both cases. The second in the case of the conductivities is then found from the observed value by multiplication by a factor.

From the portion of the figure (Fig. VII.) it is evident





that the lines representing variation of conductivity and variation of fluidity with temperature are almost coincident. That is, the temperature coefficients are almost the same in both, the difference in any case not being over eight percent, and in most cases much less than this, particularly for solutions in ethyl alcohol. Wöllmer (loc. cit.) has already called attention to this fact.

(I have already shown (p. 4\*) that this is also true for certain electrolytes of certain mixtures of solvents. Though the temperature coefficients of fluidity and conductivity are the same, the value of the quotient  $\frac{\mu\eta}{\alpha}$  is much greater for an electrolyte in the mixture than for the same electrolyte in the pure alcohol. It is difficult to see why this is the case - unless it be that in the mixture we have a complex solvent not to be compared with the simple solvent. Certainly the presence of hydrates in the mixture should complicate matters. This interesting point needs further investigation.

(Knowing the values of the constant for the pure solvent and assuming the validity of the relation for the mixture we might calculate the ionic friction. - This ionic friction would not be the same as the coefficient of viscosity of the mixture, but its variation with temperature would be the same.) This amounts, then, to a proof of the Wiedemann hypothesis.



for solutions of methyl and ethyl alcohols. And since proof is necessary to show the validity of the synthesis proposed by me.

The next step is the discussion of certain data as to conductivities in the two solvents, - proof that the expression  $\frac{\mu\eta}{x}$  holds for solutions in these solvents. The values for coefficients of viscosity have been taken directly or interpolated from the results of Thorpe and Podger<sup>(1)</sup>. The values for the conductivities in the various solvents are taken from observations of Vollmer (loc. cit.), Carrara (loc. cit.), Lindsay (loc. cit.) and others, and from my own. The values for the association factors are those given by Passay and Shields<sup>(2)</sup> in their first paper, for methyl alcohol at ordinary temperatures, 3.43, for ethyl alcohol, 2.74.

Table 69.  $\frac{\mu\eta}{x}$  for lithium nitrate in methyl and ethyl alcohols.

Volume	$\text{CH}_3\text{OH}$		$\text{C}_2\text{H}_5\text{OH}$	
	0°	25°	0°	25°
I.	0.1288	0.1238	0.1239	0.1211
II.	0.1339	0.1339	0.1388	0.1343
III.	0.1481	0.1383	0.1300	0.1402

(1). Phil. Trans. 1891, 1897, (1894).

(2). Amer. Jour. Chem. 12, 433, (1933).



The conductivities compared were for the volumes 128, 256, 512 for methyl alcohol, 198.7, 381.4, 761.8, for ethyl alcohol, these being comparable dilutions. In the case of ethyl alcohol solutions values for the conductivities were found by interpolation.

As is seen from inspection of the table, the constants for the comparable values are equal to within a few percents. Further, the constant is the same at the lower and at the higher temperature. Of course the constants are not the same for the different volumes, for here we have used the association factor as a constant in the equation. It represents dissociation, and if we were to substitute percent of dissociation for the association factor, the values for the constant would be the same in all cases.

Altogether, the agreement of theory and fact is all that could be expected, when we consider the errors involved in the determination of the quantities used. The figures for association are certainly only approximate. Conductivities are liable to an error of one percent or over, and different observers give values for the viscosity coefficients differing by as much as four or five percent.



Table 70.  $\mu_{\text{x}}$  for ammonium bromide in methyl and ethyl alcohols.

Volume	24.00 - 25°	24.00 - 0°
I	0.1369	0.1293
II	0.1441	0.1416
III	0.1513	0.1531

The volumes of comparison are the same as those in the case of lithium nitrate.

Values for the conductivities in ethyl alcohol are taken from Lindsay. Those given by Lindsay for methyl alcohol solutions are not used. Those of Carrara are taken, as they agree with values given by Zelinsky and Grapiwin (loc. cit.) while those of Lindsay do not.

In all cases agreement is as close as could be expected.





Table 71.

for potase on iodide in methyl and ethyl alcohols.  
x

	CH <sub>3</sub> OH	CH <sub>3</sub> OH	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	μH <sub>2</sub> SO <sub>4</sub>	μH <sub>2</sub> SO <sub>4</sub>
Vol- ume.	25	25	0	25	0		
	Lindsay	Carrara	Lindsay	Lindsay	Lindsay		
I	0.1377	0.1308	0.1417	0.1298	0.1359		
II	0.1471	0.1408	0.1526	0.1428	0.1479	0.510	0.571
III	0.1558	0.1466	0.1617	0.1544	0.1592	0.525	
IV	0.1636	0.1513	0.1665	0.1698	0.176	0.539	0.571
						0.539	0.571

The volumes compared were 64, 128, 256, and 512 for methyl alcohol, for ethyl alcohol, 15.7, etc. Both Lindsay's and Carrara's values for conductivities in methyl alcohol were used in order to compare the results. In some cases those of the one give better agreement, in other cases, those of the other, indicating that the differences are influenced by experimental error.

(1)  
It should be stated that it is also Gantenbeister's values for the coefficients of viscosity were used. The calculations were made before I decided to use the values given by Thorpe and Rodger. It would hardly be profitable to recal-



calate, since the result is the same, whatever figures be used. I have satisfied myself of this by numerous trials. In many cases three or four calculations have been made, using the different constants given in the tables of Landolt and Doernsteir.

Table 72.

$\frac{\mu\eta}{x}$  for lithium chloride in methyl, ethyl and propyl alcohols.

Volume	$\text{CH}_3\text{OH} - 25^\circ$	$\text{C}_2\text{H}_5\text{OH} - 18$	$n\text{-C}_3\text{H}_7\text{OH} - 15^\circ$
I.	0.1213	0.1256	0.1164
	0.1166		Völlner - $15^\circ$

The volumes compared are 256, 403, 604. The values for  $\mu\eta$  conductivities are taken from Carrara (loc. cit.) Völlner (loc. cit.) (1) and for n-propyl alcohol, from Schlamp.

The agreement is satisfactory.

It is interesting to note that the relation holds for picric acid in methyl and ethyl alcohol solution. There the volumes compared are 205 and 270 respectively,  $\frac{\mu\eta}{x}$  in the one case equals 0.0665, and in the other, 0.0641. The data for the comparison are furnished by Schall (2).

(1). Ztschr. Phys. Chem. 14, 274, (1894).

(2). Ztschr. Phys. Chem. 14, 707, (1894).



Other results may be summarized without going further into details.

Table 73.

$\frac{\mu\eta}{x}$  for various electrolytes in different solvents.

	CH <sub>3</sub> OH	C <sub>2</sub> H <sub>5</sub> OH	n. C <sub>3</sub> H <sub>7</sub> OH
NaI	0.1438	0.1447	Carroll (25°) - Völlmer (18°).
$v = 200$ & 283			
$v = 750$ & 575	0.157		0.159 Carroll (25°) - Schlamp (15°).
NaO <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	0.1156		Völlmer (18°)
$v = 832$ 1200	0.1123	0.1093	Carrara (25°) - Völlmer (18°)
KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	0.1279	0.1247	Völlmer (18°)
NaCl			
$v = 228$ 340	0.1457	0.1366	Carrara (25°) - Völlmer (18°).

In all these cases the agreement continues to be satisfactory.

In the foregoing pages I have discussed all the material available in the literature. In all of the cases - some nine in number - fact and theory are in accord. It must be admitted that the proposed hypothesis thus holds as a highly probable one. Further investigation is, however, desirable, to



see how widely it applies.

For solutions in which dissociation is complete the formulated hypothesis becomes  $\gamma = 1$ . The proof of the validity of this relation is, it seems to me, a crucial test. It gives in the following table the necessary comparisons.

Table 74.  $\gamma$  for various electrolytes in various solvents.

Electrolyte	$C_2H_5OH$ $n=0.012385$ 18°	$C_2H_5OH$ $n=0.00666(18^\circ)$ 0.00552(25°)	$CH_3CO.CH_3$ $n=0.00353$ 25°	$nC_3H_7O$ $n=0.002634$ 18°
KI	0.567	0.530-18 0.528-25	0.541	
NaI	0.466	0.505-18 0.496-25	0.434	0.421
$NH_4I$		0.581	0.538	
LiCl	0.377	0.416-18 0.427-25		0.31
NaCl	0.434	0.479		

(1)

The values for acetone were taken from Garrara, those for ethyl alcohol from Vollmer (loc. cit.), those for methyl alcohol from Vollmer and from Garrara (loc. cit.), and those for propyl alcohol from Scalap (loc. cit.)

(1). Gazz. Chim. Ital. 27 (1), 217, (1897).





When we consider the necessarily large experimental error involved in the determination of the limiting values for conductivity - an error that must certainly be greater than that involved in the determination of conductivities at ordinary dilutions - the agreement is as good as could be expected. Further, for lithium and sodium chlorides in ethyl alcohol limiting values were probably not reached, for with them Voller did not go to a dilution as high as in other cases. The constants for these salts would probably be greater than the values given in the table, thus making the agreement better.

#### Summary and Conclusions.

- I. The work of Zelinsky and Krapivin and of Lindsay has been extended, and the occurrence of the minimum in conductivity has been shown in three cases - cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water.
- II. The dissociation (as determined from conductivity) of sodium and potassium iodide and potassium bromide, has been determined for 50% methyl alcohol and has been found to be greater than that in water at the corresponding dilution.
- III. It has been shown that the explanation of the minimum



in conductivity offered by Lindsay cannot be the correct one. The phenomenon has been shown to be dependent upon the decrease in fluidity resulting on mixing the components of the electrolyte.

II. The hypothesis of Dutoit and Aston has been proved quantitatively for certain salts in three solvents - water, methyl alcohol and ethyl alcohol.

V. The hypothesis of Kohlrausch (formation of an atmosphere of the solvent around the ions in solution) has been shown to hold for binary electrolytes in methyl and ethyl alcohols.

VI. A hypothesis correlating conductivity, association and viscosity (or fluidity-) has been proposed, and has been shown to hold for all cases available for discussion.



ALABAMA.

The author of this dissertation, Charles Walter Carroll, was born in Ashland, Kentucky, on October 15, 1875.

His preparatory training was received in the public schools of Pueblo, Colorado, and in the Preparatory Department of the University of Denver. In 1890 he entered the freshman class of the University of Denver, where he continued a year. The next three years were spent in teaching in the state of Texas. In the fall of 1896 he entered the Southwestern University, at Georgetown, Texas, receiving the B. A. degree in 1896, and the M. A. degree in 1897. Since graduation he has been connected with that institution, being at present professor of Chemistry.

In the fall of 1901 he entered the Johns Hopkins University as a graduate student in Chemistry and has been in attendance during the years 1901-2 and 1903-4. His subordinate subjects were Physical Chemistry and Physics.















